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OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. XVIII.—NO. 11.

NOVEMBER, 1896.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,

COMMITTEE ON PAPERS AND PUBLICATIONS.

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PAPERS ACCEPTED FOR PUBLICATION:

The Action of Acid Vapors on Metallic Sulphides. By Jerome Kelley, Jr., and Edgar F. Smith.

Tungsten Hexabromide. By Herbert A. Schaffer and Edgar F. Smith.

Notes on the Ferrocyanides of Zinc and Manganese. By Edmund H. Miller.

The Behavior of Coal-Tar Products toward the Process of Digestion. By H. A. Weber.

A Modified Form of the Ebullioscope. By H. W. Wiley.

Carbon Determinations in Pig Iron. By Bertrand S. Summers.

Metal Separations by Means of Hydrochloric Acid Gas. By J. Bird Moyer.

The Separation of Bismuth from Lead. By Arthur L. Benkert and Edgar F. Smith.

The Atomic Weights of Nitrogen and Arsenic. By Joseph Gillingham Hibbs.

The Separation of Manganese from Tungstic Acid. By Walter T. Taggart and Edgar F. Smith.

Mineral Constituents of the Watermelon. By George F. Payne.

The Separation of Vanadium from Arsenic. By Charles Field, 3rd, and Edgar F. Smith.

Issued with November Number, 1896.

Proceedings.

COUNCIL.

By direction of the Council a congratulatory address was forwarded to Stanislas Canizzaro, an honorary member of this Society, upon his seventieth birthday.

December 29 and 30 has been selected as the date for the annual meeting at Troy, N. Y.

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MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The first meeting for the year 1896–97 was held at Providence, on Thursday evening, September 24th, Chairman E. D. Pearce presiding.

Prof. J. H. Appleton read a paper upon the "Electrolysis of Salt."

The introduction to this paper was a brief discussion of the present chemical application of electricity. First in importance at present is the preparation of metals, copper, gold from cyanide solutions, zinc, glucinum, and even some more difficultly reducible metals or non-metals; sodium, lithium, cadmium, cobalt, nickel, and phosphorus. Next, reference was made to the production of certain compounds in which primarily the heat of the current is involved: silicon carbide, calcium carbide, as well as those metallic carbides, produced by Moissan, which, with water, yield such varied hydrocarbons (very suggestive in relation to the origin of petroleum).

The electrolysis of salt by several methods, notably Castner's, was next taken up.

In conclusion, there were presented some comments on the probable influence of the electrolysis of salt on the alkali industry.

NEW YORK SECTION.—ANNUAL MEETING.

OCTOBER 9, 1896.

The meeting was called to order at 8.20 P. M., by Dr. P. T. Austen, Chairman.

In the absence of the secretary, Dr. A. C. Hale was appointed secretary *pro tem.*

The minutes of the meeting held June 8th, 1896, were read and approved.

Reports of officers and committees being in order, the chairman called upon Dr. Hale to report for the delegates to the Scientific Alliance of New York. Dr. Hale made a brief oral report, which was accepted.

Dr. P. T. Austen, the retiring chairman of the section, reported on the work of the year and the general condition and prospects of the section and the society as well as the outlook for American chemists generally.

After these remarks by the retiring chairman the election of officers of the section for the ensuing year was held.

Dr. Durand Woodman was unanimously elected secretary and treasurer. Other officers were elected unanimously, as follows:

Chairman—Dr. Wm. McMurtrie.

Executive Committee—Dr. Charles A. Doremus, Prof. A. A. Breneman, Dr. Albert C. Hale.

Delegates to the Scientific Alliance of New York—Dr. Wm. McMurtrie, Dr. C. F. McKenna, Dr. C. A. Doremus.

Dr. Wm. McMurtrie, chairman-elect, then took the chair, and upon motion of Dr. Doremus, a vote of thanks to the retiring chairman was passed unanimously.

Prof. Breneman reported very encouraging progress in reference to the proposed chemical club.

Papers were read and discussed as follows: "Some Disputed Points about the Light of Carbon," by Woodbridge H. Birchmore; discussed by Prof. Speyers, Mr. Birchmore, and Mr. Stillwell. "The Conversion of Cow Milk into a Substitute for Human Milk," by Henry A. Bunker; discussed by Dr. Eccles, Dr. Bunker, and Dr. McMurtrie.

Upon motion of Dr. Doremus, seconded by Dr. Squibb, the following named persons were appointed a committee to cooperate with other scientific bodies in New York for the purpose of securing a lecture from Prof. Henri Moissan before his return to

France: C. A. Doremus, A. A. Breneman, M. Loeb, and Wm. McMurtrie.

Upon motion of Dr. Hale, the chairman of the section was authorized and requested to appoint a committee, with himself as chairman, to arrange the programs for the meetings of the section during the year.

The meeting then adjourned.

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A NEW FORM OF POTASH BULB.[1]

BY M. GOMBERG.

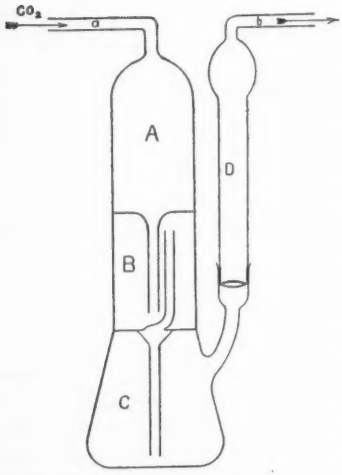
Received August 28, 1896.

THE potash bulb most frequently used at present in elementary organic analysis is that known as Geissler's bulb. While neat and compact, it still has the same drawback as possessed by other forms of potash bulbs; namely, that even with the most careful handling it is not unfrequently broken. Some two years ago I drew up a design for a different form of bulb, wherein all the connections should be enclosed. Several attempts to have it made in this country have proven unsuccessful. The design was then sent to Greiner & Friedrichs, of Thüringen, and I have recently received from them samples of such bulbs. Meanwhile, it came to my notice that a bulb based on similar principles has been put upon the market by Bender & Hobein, of München. A comparison of the two bulbs shows them, however, to be sufficiently different to justify me in presenting a description of the one made according to my design, without claiming priority as to the principle of construction.

The arrangement and working of the bulb will appear clear from the subjoined diagram, which presents the apparatus reduced to one-half its actual size.

The potash bulb is divided into three compartments, *A*, *B* and *C*. *B* and *C* contain the potash solution for the absorption of the carbon dioxide, while *A* serves as a safety reservoir in case of backward suction. The bulb is filled by dipping *a* into the solution, and applying suction at *b*, until the two com-

[1] Communicated by A. B. Prescott. Read at the meeting of the American Chemical Society, Buffalo, N. Y., August 22, 1896.



partments *B* and *C* contain as much of the solution as would completely fill *A*, which is about thirty-five to forty grams of a 2 : 3 solution. *D*, which is fastened to the bulb by means of a ground-glass joint, contains solid potassium hydroxide, or soda-lime, supported by a plug of glass-wool. The liquids in *B* and *C* can be easily mixed when desired, by applying suction at *a*. The bulb, when filled and ready for use, weighs from sixty-five to seventy grams, and undoubtedly can be made even much lighter.

The total number of compartments is thus reduced from five in Geissler's form to three in the form here presented, while the absorbing chambers are reduced only from three to two. The construction of the bulb is such that *C* can never get overfilled by the solution from *B*.

This form of a potash bulb possesses the advantages first, that it can be easily handled and wiped, presenting the outside surface of an ordinary small flask, and second, that it can be set without any support, and can be weighed without suspending it if so desired.

I wish to express my thanks to the firm of Greiner & Friedrichs, of Thüringen, who have kindly made the bulb for me in a most satisfactory manner.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.

REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

Received August 27, 1896.

IN a previous communication[1] the writer noted that copper was acted upon by concentrated sulphuric acid (1.84 sp. gr.) not

[1] This Journal, 17, 90.

only at the ordinary temperatures of the air, 20°–30° C., but at zero as well. Andrews[1] states that the assertion is incorrect and that it does not occur until the temperature 86° C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67° C., according to him. Andrews further says that the author's statements were based "not upon any demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86° C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of the results in this paper.

As far back as 1834 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel.[2] Calvert and Johnson,[3] however, failed to obtain any action below 130° C. and considered that none took place. Pickering,[4] however, stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3–4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to

[1] This Journal, **18**, 253.
[2] *J. de pharm.*, **20**, 13, *1834*.
[3] *J. Chem. Soc.*, **19**, 438, *1866*.
[4] *J. Chem. Soc.*, Trans., *1878*, 113.

the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews[1] states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O.''$$

Formerly the author[2] stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené[3] proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly exposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above, the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should be a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra internal pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate

[1] This Journal, **18**, 252.
[2] *Ibid*, **17**, 912.
[3] *Ann. chim. phys.*, *1846*, [3], **18**, 311.

solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second Experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°–30° C.

Third Experiment.—An ordinary Kjeldahl digestion flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued

observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr., is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews[1] was employed with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with the permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were also formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.[2] In stating the results, however, the author gave the temperature as "0°–10° C." The flask

[1] This Journal, **18**, 251.
[2] *Ibid.*, **17**, 908.

containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0°–10° C., however. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except with regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

UNIVERSITY OF NORTH CAROLINA.

THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.

BY L. M. DENNIS.

Received September 4, 1896.

SOME time ago the author and F. L. Kortright[1] briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

[1] *Ztschr. anorg. Chem.*, **6**, 35; *Am. Chem. J.*, **16**, 79.

The solution of potassium trinitride which was used was prepared by carefully neutralizing a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about three and two-tenths grams of potassium trinitride to the liter.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0°, and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing one per cent. hydrochloric acid, and was then dropped into a hot, concentrated solution of ammonium oxalate. It dissolved completely and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of ten cc. each with ammonium hydroxide, filtering, washing, igniting, and weighing as ThO_2. Two determinations gave, for thorium oxide in ten cc., 0.0591 gram and 0.0595 gram. The mean of these results is equivalent to 0.00521 gram thorium in one cc.

Upon adding to this thorium solution a few cc. of the solution

of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white, flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odor of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as ThO_2. Twenty cc. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0.1186 gram thorium dioxide gave, by precipitation with potassium trinitride, 0.1183 gram thorium dioxide, equivalent to 0.00520 gram thorium in one cc. instead of 0.00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two hole rubber stopper, through one opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0.0075 gram thorium in one cc., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two

minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute, hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten cc. of thorium nitrate and ten cc. of potassium trinitride were used. The silver chloride resulting weighed 0.1447 gram, equivalent to 0.0434 gram hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

5 cc. gave 0.0744 AgCl = 0.02232 HN_3,
5 cc. gave 0.0745 AgCl = 0.02235 HN_3.

Using the mean of these results, it appears that 0.0446 gram of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0.0434 gram was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilization during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation

$$Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4HN_3.$$

This reaction is interesting not only because of the quantita-

tive precipitation of thorium by this means, but also because of the peculiar behavior of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behavior of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating, into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as La_2O_3. The solution contained 0.00431 gram lanthanum in one cc. This solution gave no precipitate when boiled for some minutes with potassium trinitride. Fifteen cc. of this solution and fifteen cc. of the thorium chloride solution were placed in an Erlenmeyer flask, twenty-five cc. of potassium trinitride (three and two-tenths grams to the liter) was added and the solution was boiled for one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate five cc. more of potassium trinitride was added and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia and the lanthanum weighed as the oxide. The results were:

	Taken.	Found.
Thorium	0.0781	0.0777
Lanthanum	0.0646	0.0642

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot, concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink color and absorption bands of didymium and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate which was filtered off. By precipitation with ammonia this solution of cerium, lanthanum, didymium, etc., free from

thorium, was found to contain 0.0166 gram of the mixed oxides in one cc. The precipitation was made as in the separation from lanthanum and an excess of potassium trinitride was used in each case.

		Taken.	Found.
I.	Thorium	0.1300	0.1294
	Ce, La, Di oxides	0.0332	....
II.	Thorium	0.0785	0.0783
	Ce, La, Di oxides	0.0830	....
III.	Thorium	0.0535	0.0526
	Ce, La, Di oxides	0.2490	....
IV.	Thorium	0.0535	0.0531
	Ce, La, Di oxides	0.2490	....
V.	Thorium	0.0550	0.0541
	Ce, La, Di oxides	0.4980	....
VI.	Thorium	0.0555	0.0550
	Ce, La, Di oxides	0.5810	....
VII.	Thorium	0.0570	0.0558
	Ce, La, Di oxides	0.8300	....

The recovery of the thorium is in all cases fairly exact and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.

CORNELL UNIVERSITY, August, 1896.

NOTES ON REINSCH'S TEST FOR ARSENIC AND ANTIMONY.

By Jas. Lewis Howe and Paul S. Mertins.

Received September 12, 1896.

THAT Reinsch's test for arsenic possesses, in point of convenience, marked advantages over that of Marsh, is generally acknowledged, but it has been questioned both as to delicacy and as to accuracy in distinguishing between arsenic and antimony. As to the former point, Reinsch, in his second article on the test,[1] states that arsenic may be detected in a solution of one part per million. In his original description[2] of the test he placed the accuracy about one-third of this. Our own experiments show that this accuracy is not overstated. The fact that arsenious oxide and antimonous oxide (Sb_2O_3) are isomorphous in their crystallization has led to the conjecture that antimonous oxide subliming from the copper in the closed tube might appear in the brilliant octahedra, characteristic of arsenic in the test.

Experiments bearing on this point were made as follows:

Reinsch's test was applied to the different compounds of arsenic in this laboratory and in each case several sublimation tubes were used. The test was carried out by boiling the substance with sixteen per cent. hydrochloric acid, in which several strips (2.5 × 0.5 cm.) of thin, pure copper were placed. After fifteen minutes (except in cases to be mentioned later) the strips of copper were removed, washed and dried, and after rolling or folding to small compass, placed in open tubes five cm. long and not over five-tenths cm. diameter. These tubes were held in an inclined position in the lowest possible flame of a Bunsen burner until the arsenic sublimed; a second or two usually suffices.

The test was similarly carried out with compounds of antimony and also with various organs of two cats, one killed by six grains of tartar emetic, dying six hours after administration, and the other dying in three days after the administration of the first of six small doses given every twelve hours. Each dose was two grains, but much of this was probably not taken into the system. A perceptibly higher degree of heat was necessary to

[1] H. Reinsch: De l' Essai de l' Arsenic par le Cuivre: *J. pharm. Chim.*, **2**, 361, (*1842*).

[2] H. Reinsch: Ueber das Verhalten des metallischen Kupfers zu einigen Metallösungen: *J. prakt. Chem.*, **24**, 244, (*1842*).

sublime the antimony than was the case with arsenic; altogether 185 tests were made, most of them furnishing good sublimation tubes. Each tube was numbered as made, and later the whole number were mixed and sorted for arsenic and antimony by examination with a microscope of low power. Reference to the note book showed that in no case had a mistake been made, in fact in every case the arsenic sublimation could easily be distinguished from that of antimony by the naked eye. In no case did the sublimate of antimonous oxide show a trace of crystallization under the microscope used, nor did the arsenious oxide fail in any case to show the characteristic brilliant octahedral crystals.

The evidence that the antimonous oxide cannot appear in crystals which might be mistaken for arsenic is of course negative, but owing to the variety of forms used it must be considered to have the weight of positive evidence.

As regards the substances tested, the following may be recorded:

All arsenious compounds soluble in hydrochloric acid gave the deposit on copper immediately on heating.

Commercial "metallic" arsenic gave the deposit readily.

Freshly sublimed "metallic" arsenic (bright crystals) gave no deposit.

Arsenates gave a deposit only after several minutes boiling.

In the presence of nitric acid or chlorates no test is obtained owing to the solution of the copper.

Whenever aqua regia or potassium chlorate is necessary for solution of an arsenic compound, the solution should be evaporated to dryness with hydrochloric acid. The test can then be carried out as with arsenates.

The presence of organic matter in the arsenic solution does not affect the test, hence it can be applied directly to any organs without any previous destruction of tissue. If much arsenic is present it is best to use but a small portion of the substance, since if much arsenic is deposited on the copper, it will not adhere with firmness.

Antimony is not precipitated on the copper as rapidly as arse-

nic, and the deposit has a decidedly violet tint, very distinct from the iron gray deposit of arsenic.

The following distribution of antimony in the two cats may be added :

	Acute poisoning (6 hours).	Slow poisoning (72 hours).
Stomach.	Heavy deposit and sublimate. Good test with $\frac{1}{100}$ of stomach.	Good tests.
Liver.	Not so heavy deposit as stomach. Good sublimate.	Heavy deposit and good sublimate.
Heart.	Good deposit after several hours boiling. Good sublimate.	Good deposit on ninety minutes boiling. Good sublimate.
Pancreas.	Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Spleen.	Faint deposit. No distinct sublimate.	
Kidney.	Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Intestine.	Good deposit and sublimate.	Good deposit and sublimate.
Muscle.	Faint deposit on two days boiling. No sublimate.	Slight violet tinge to copper. No sublimate.
Brain.	No deposit.	Marked violet tint to copper. No sublimate.
Spinal Chord.	No deposit.	

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NOTES ON THE DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.

BY GEORGE AUCHY.

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OF the many improvements made in recent years in the method of determining phosphorus in steel, that of Jones —the use of the "reductor"—is not the least. There has been, however, some difference of opinion as to the completeness of the reduction accomplished by its use. Quoting from three most recent publications on the subject: Doolittle and Eavenson consider the reduction of the molybdic acid to be to a point cor-

responding to the ratio of 89.16 iron to molybdic acid; Noyes and Royse, by special precautions, obtain a reduction completely to Mo_2O_3 (factor 85.71); and Blair and Whitfield find the ratio 88.16, a reduction to $Mo_{24}O_{37}$ only, even with the precautions of Noyes and Royse observed. Doolittle and Eavenson heat the solution before passing it through the reductor. Noyes and Royse do not. The first named chemists do not use the precautions of Noyes and Royse. It appears from a result by Prof. Noyes given in this Journal, **10**, 759, that he does not invariably get a reduction to Mo_2O_3 by his method, his result there given corroborating Blair and Whitfield's hypothesis of a reduction to $Mo_{24}O_{37}$ only.

It was thought by the writer that perhaps the reduction to Mo_2O_3 could invariably be accomplished by combining the precautions of Noyes and Royse with the practice of Doolittle and Eavenson of passing the solution through the reductor hot. The following results were obtained, using yellow phosphomolybdate precipitate dried six hours at 150° C.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0100	1.63	1.63	1.68
0.0100	1.63	1.63	1.68
0.0200	1.63	1.59	1.63
0.0300	1.63	1.63	1.68
0.0300	1.63	1.61	1.65
0.0200	1.63	1.55	1.59
0.0400	1.63	1.59	1.63
0.0500	1.63	1.62	1.67
0.0500	1.63	1.63	1.68
0.0600	1.63	1.63	1.68
0.0700	1.63	1.61	1.65
0.0700	1.63	1.60	1.64
0.1000	1.63	1.63	1.68
0.0400	1.63	1.59	1.63
0.0400	1.63	1.59	1.63
0.0200	1.63	1.58	1.62
0.0400	1.63	1.56	1.60
0.0300	1.63	1.59	1.63
0.0900	1.63	1.57	1.61
0.0400	1.63	1.60	1 64
0.0500	1.63	1.61	1.65

Passing the solution through the reductor hot does not seem to insure an invariable reduction to Mo_2O_3, and perhaps adds nothing to the effectiveness of the process. The following tests were made in the cold :

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.58	1.62
0.0400	1.63	1.59	1.63
0.0300	1.63	1.59	1.63
0.0400	1.63	1.57	1.61
0.0500	1.63	1.63	1.68

But in these last tests, and also in the first series of tests in nearly all cases where the result calculated by Noyes' factor came low, the point of the reductor had been washed off, and the sides of the flask washed down by the jet. Noyes warns against any dilution of the reduced solution before titration, but it was thought that such a slight dilution would do no harm. For a test of this the following determinations were made (cold) and without washing down :

Phosphomolybdate taken. Gram.	Phosphomolybdate present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.61	1.65
0.0900	1.63	1.60	1.64
0.0300	1.63	1.61	1.65
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0500	1.63	1.62	1.67

Comparing these results with those of the preceding series it is seen that a complete avoidance of any dilution, however slight, after reduction, will bring higher results than if this precaution be neglected. But it is further seen that the observance of this precaution does not invariably assure a result agreeing with a reduction to Mo_2O_3, although it generally does so. Of the eleven results in the first series of experiments (solution passed through the reductor hot), obtained by an observance of this precaution, seven, calculated by Noyes' factor, are over 1.61 ;

and of the ten results of the last series (reduced cold), seven are 1.61 per cent. or over. On the other hand, of the thirteen results obtained by washing down the sides of the flask after reduction, ten fall short of the theoretical 1.63 per cent. by more than 0.02 per cent., calculated by Noyes' formula, and do bring 1.63 per cent. calculated by Blair's factor. The inability of Messrs. Blair and Whitfield to accomplish a reduction to Mo_2O_3 by an observance of the precautions given by Messrs. Noyes and Frohman, and also the still higher factor found by Messrs. Doolittle and Eavenson, may perhaps be due to the fact that the zinc in each case used differed in reductive power from that of the others. The writer had on one occasion zinc which when used in the reductor with all care and precautions, never gave a reduction of more than one-half; and in his opinion it is safer and more accurate to use the old Emmerton method of reduction and filtration, but with the modifications and precautions described later in this article.

The phosphomolybdate employed in the above tests, was, for part of them, made by precipitating from sodium phosphate solution; for another part of the tests, made by precipitation from pig iron solution, exactly as is done in the determination of phosphorus in pig iron. Messrs. Blair and Whitfield have shown the constancy of the composition of phosphomolybdate made under varying circumstances.

The volume of the solution passed through the reductor in each of the above experiments was 100 cc., as recommended by Blair and Whitfield. Noyes and Frohman use 200 cc., but this seems an unnecessary bulk. Fifteen cc. of sulphuric acid (2:1) was used for acidifying.

For washing 100 cc. of hot water was used containing ten cc. of sulphuric acid, (2:1), followed by 100 cc. cold water, and again by fifty to seventy-five cc. of cold water.

The reductor was of the form described by Blair and Whitfield,[1] except that it was considerably wider at the top than the bottom—in shape like a common tin horn. This shape holds more zinc for the given height (ten inches) of the column, and so makes the necessity of filling less frequent.

[1] This Journal, 17, 74.

The reductor may be used without refilling till the column of zinc falls to five or six inches without any diminution of effectiveness. All of the results of the two preceding series, and some of the last results in the first series were obtained by the use of five to seven inches of zinc in the reductor.

It adds somewhat to the facility of the working of the apparatus to have the beaker containing the phosphorus solution above the level of the zinc in the reductor so that the connecting tube may work as a siphon. And the last washing may then conveniently be made by diminishing the force of the suction of the pump, loosening the stopper of the reductor, and allowing the water to be siphoned over and fill up the vacant space in the reductor above the zinc column.

The passage of the solution through the reductor was not preceded by the passage of dilute sulphuric acid, and in many of the tests some little air was accidentally drawn over into the reductor at the time of washing, although care was uniformly taken to allow no air to enter at the first washing.

Messrs. Noyes and Royse direct that the reductor should be rinsed with dilute sulphuric acid before using, even if it has stood but a few minutes. This is some little trouble, and to test the necessity of it, the following tests were made :

Phosphomolybdate taken. Gram.	Phosphorus taken. Per cent.	Phosphorus found. Per cent.	Reductor stood.
0.0300	1.63	1.61	one hour
0.0700	1.63	1.60	all night
0.1000	1.63	1.63	six hours
0.0300	1.63	1.63	all night
0.0300	1.63	1.63	three hours
0.0300	1.63	1.63	two days
0.0300	1.63	1.63	two days
0.0500	1.63	1.63	two days
0.0500	1.63	1.62	two days

These results seem an indication that this precaution is not absolutely necessary. But if the reductor stand nearly a week or more, the sulphuric acid will take up considerably more of the impurity of the zinc than ordinarily. Zinc, for instance, which ordinarily will require a deduction of two-tenths cc. from the amount of permanganate used in the titration, will require

a deduction of four-tenths if the reductor has stood that length of time unused.

It is necessary to remove the zinc from the reductor at intervals for cleaning, best done by stirring up in a capacious dish with hot water, adding a little sulphuric acid to clear the liquid, pouring off, washing by decantation and drying in the dish on the hot plate. But after such a treatment the zinc, after being replaced in the reductor, should be rinsed with dilute sulphuric acid before being used in analysis, as much more than the ordinary impurity of the zinc will be taken up by the sulphuric acid the first time it is used.

Perhaps a more convenient way of cleaning the zinc is to soak it (in the reductor) in water for a day (conveniently over Sunday), plugging up the ends of the reductor to retain the water. After such a treatment the reductor will go a long time without becoming clogged up with zinc oxide.

Instead of using the reductor, it is a trifle quicker and more convenient, especially when the phosphorus present is considerable as in pig iron, to use the following slight modification of the old Emmerton method of reduction and filtration.

The yellow precipitate in a seven cm. filter paper is dissolved in as little ammonia as possible, allowing to run into the eight-ounce Erlenmeyer flask in which the precipitation occurred; washed five minutes with hot water; the solution acidified with twenty-five cc. of sulphuric acid (two parts water to one part acid); a mustard spoonful of granulated zinc added (five grams), and the flask heated *gently* on the hot plate for five minutes, or until the zinc is nearly dissolved (ten minutes is required for some zinc). The flask is removed from the plate, a little dry sodium carbonate added, and when effervescence has nearly ceased the flask is corked tightly and cooled in cold water without agitating the contents any more than can be helped. The solution is then filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel, smallest size, using the pump, and the flask rinsed out with cold water three times and the rinsings drawn through the cotton wool. The sides of the sixteen-ounce gas flask which receives the liquid are washed down with the jet, and the solution titrated in the flask without further dilution.

If the zinc is of the sort not dissolving very readily, thirty-five cc. of sulphuric acid should be used for acidifying the phosphorus solution instead of twenty-five cc.

The reduction is to $Mo_{12}O_{19}$. Factor of iron to molybdic acid 90.76. More correctly speaking, the reduction is to Mo_2O_3, which filtering and dilution oxidizes to $Mo_{12}O_{19}$.

It will be found upon trial that this way of reduction and filtration is somewhat easier and more rapid than the usual reductor method, as the filtration through cotton wool in a Hirsch funnel and with aid of the pump is performed as easily and quickly as merely pouring and rinsing from one vessel into another. While the zinc is dissolving in one determination, the yellow precipitate of the next determination may be filtered off.

The following results show that the reduction and filtration through cotton wool, as described, brings the molybdenum oxide to the form $Mo_{12}O_{19}$.

Considerable phosphomolybdate (four-tenths to eight-tenths gram) taken for each test.

Phosphorus present.	Phosphorus found. Factor 90.76.	Phosphorus present.	Phosphorus found. Factor 90.76.
Per cent.	Per cent.	Per cent.	Per cent.
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62
1.63	1.62	1.63	1.63
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62

Small amounts of phosphomolybdate taken.

Phosphomolybdate taken.	Phosphorus present.	Phosphorus found. Factor 90.76.	Phosphorus present, reckoned as if from 1.8233 grams steel.	Phosphorus found if from 1.8233 grams steel.
Gram.	Per cent.	Per cent.	Per cent. in the steel.	Per cent. in the steel.
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.65	0.179	0.181
0.2000	1.63	1.63	0.179	0.179
0.1500	1.63	1.64	0.134	0.135
0.0890	1.63	1.62	0.071	0.071
0.0700	1.63	1.64	0.062	0.063
0.0700	1.62	1.63	0.062	0.062

Phosphomolybdate taken.	Phosphorus present.	Phosphorus found. Factor 90.77.	Phosphorus present, reckoned as if from 1.8233 grams steel.	Phosphorus found if from 1.8233 grams steel.
Gram.	Per cent.	Per cent.	Per cent. in the steel.	Per cent. in the steel.
0.0600	1.63	1.64	0.054	0.054
0.0600	1.63	1.63	0.054	0.054
0.0500	1.63	1.61	0.045	0.044
0.0400	1.63	1.64	0.036	0.036
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.61	0.027	0.027
0.0300	1.63	1.60	0.027	0.026
0.0400	1.63	1.62	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0350	1.63	1.62	0.031	0.031
0.0380	1.63	1.63	0.034	0.034
0.0250	1.63	1.61	0.022	0.022
0.0230	1.63	1.61	0.020	0.020
0.0200	1.63	1.55	0.018	0.017
0.0200	1.63	1.51	0.018	0.017
0.0200	1.63	1.64	0.018	0.018
0.0200	1.63	1.50	0.018	0.017
0.0200	1.63	1.60	0.018	0.018
0.0200	1.62	1.55	0.018	0.017
0.0200	1.63	1.57	0.018	0.017
0.0180	1.63	1.55	0.016	0.015
0.0150	1.63	1.55	0.013	0.013
0.0150	1.63	1.55	0.013	0.013
0.0130	1.63	1.51	0.012	0.011
0.0120	1.63	1.63	0.010	0.010
0.0100	1.63	1.51	0.0089	0.008
0.0100	1.63	1.55	0.0089	0.0085
0.0100	1.63	1.46	0.0089	0.008
0.0100	1.63	1.64	0.0089	0.0089
0.0100	1.63	1.64	0.0089	0.0089

The figures in the last two columns were obtained by reckoning as though 1.8233 grams of steel had in each case been taken for analyses. In other words, these percentages in the last two columns are what they would have been had the phosphomolybdate taken been, in each case, obtained from 1.8233 grams of steel, in the regular course of analysis, for phosphorus.

It will be noticed that when the amount of phosphomolybdate

taken is very small (equivalent to 0.008 to 0.017 per cent. in steel) there is frequently some oxidation, the percentage of phosphorus in the yellow precipitate thus falling short of 1.63 by as much as 0.17 per cent. in one case. But, as will be seen by reference to the last two columns of results, this affects the result in steel but slightly.

This proneness to oxidation when very little phosphorus is present in the solution indicates that the stability of the $Mo_{12}O_{19}$ solution is greater when concentrated than when dilute. And the solution should therefore be in as small bulk as possible. Other necessary precautions are: to have a large excess of sulphuric acid present, to avoid a boiling temperature when dissolving the zinc, to cool the liquid before filtering from the undissolved zinc, to exclude air while cooling, and to filter rapidly through cotton wool in a Hirsch funnel, with aid of the pump. But where considerable phosphorus is present, as in pig irons, these precautions may be neglected, except the cooling before filtering. That is, the liquid may be cooled, after the reduction with zinc, without the addition of sodium carbonate, and with free access of air, and the filtration may be made through a seven cm. coarse paper (instead of cotton wool) by aid of the pump. The results given under the head "considerable phosphomolybdate taken for each test" were obtained in this way, air not excluded, and filtered through paper instead of cotton wool.

The advantage of making the reduction and filtration in this way in the case of pig iron is very marked when, as frequently happens, the yellow precipitate separates out when its solution in ammonia is acidified with sulphuric acid. For if the reduction be made as described, this separation may be ignored as in contact with the zinc and sulphuric acid the yellow precipitate becomes reduced and goes into solution. This is shown by the following tests, in which no ammonia was used at all. That is, the yellow phosphomolybdate precipitate was weighed directly into the reducing flasks, and thirty-five cc. of sulphuric acid (2:1) poured over, a mustard spoonful of zinc added, heated gently, etc.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
About 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63

In experimenting with this process some interesting results were had. The port wine $Mo_{12}O_{19}$ solution is apparently not so stable, especially in dilute solution or with small amounts of phosphorus present, as Emmerton supposed, and certain precautions are necessary.

In the first place considerable amounts of phosphomolybdate were taken, dissolved and reduced as described, and filtered through seven cm. filter papers by aid of the pump. The results showed 1.63 per cent. phosphorus, the theoretical amount.

Several tests were then made in the same way and with the same weights of yellow precipitates, but not waiting for the solutions to cool before filtering from the undissolved zinc. Instead of the theoretical 1.63 per cent., 1.57 per cent., and 1.58 per cent. were obtained, showing the necessity of filtering cold.

Next the stability of the reduced solution was tested.

Before filtering from the undissolved zinc.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
Stood two hours	1.63	1.59
" " " and poured back and forth four times	1.63	1.55
Stood one hour	1.63	1.59
" one-half hour	1.63	1.61

The flasks were not corked while standing.

Smaller weights of phosphomolybdate precipitate were then taken. The results obtained fell very much short of the theoretical, 1.63 per cent., and varied considerably. It was at first thought that the filtration by aid of the pump oxidized the solutions more than by the original Emmerton way of filtering through a large ribbed filter. But, upon making four tests and filtering in that way (Emmerton's) the results gave 1.51 per cent., 1.52 per cent., 1.46 per cent., and 1.48 per cent., respectively, instead of the theoretical, 1.63 per cent., although about

four-tenths gram yellow precipitate, was in each case taken; an amount of yellow precipitate which, when taken for the foregoing tests made by filtering through a seven cm. filter paper by aid of the pump, never failed of bringing a result equal to the theoretical. In filtering through a seven cm. filter by the pump the oxidation of the solution is therefore considerably less than the oxidation by filtering through a large ribbed filter.

An article by Blair and Whitfield[1] contains a description of an experiment made by reducing the phosphorus solution by boiling with zinc, keeping an atmosphere of hydrogen continually in the flask, and boiling till the zinc was completely dissolved; then cooling (maintaining the atmosphere of hydrogen in the flask) and titrating, the result falling considerably below the theoretical. In the case of the writer's low results just spoken of, obtained by filtering through a seven cm. filter paper by suction, the reduction had also been effected by boiling with the zinc, though not in an atmosphere of hydrogen, and not to complete solution of the zinc. Remembering the experiment of Blair and Whitfield, above quoted, it was thought that the reason for the low results in both cases lay, perhaps, in the boiling of the phosphorus solutions while being reduced, the sulphuric acid having an oxidizing effect perhaps in that case. No other reason could be offered at least for the low result in Blair and Whitfield's experiment, since, in that experiment, air had been so carefully excluded from the flask during the solution of the zinc and the cooling of the liquid. To test the matter, other determinations were made exactly as before, except that the zinc was dissolved at a gentle heat instead of by boiling. Results were much better, as will be seen in the following table. Hence the necessity for the precaution of avoiding a boiling temperature while dissolving the zinc.

Phosphorus present—1.63 per cent.

[1] This Journal, 17, 757.

Phosphomolybdate taken. Gram.	Zinc dissolved by boiling. Phosphorus found.	Zinc dissolved at a gentle heat. Phosphorus found.
0.0100	1.37	1.55
0.0200	1.37	1.50
0.0200	1.37	1.41
0.0300	1.31	1.46
0.0300	1.37	....
0.0400	1.46	1.55
0.0500	1.39	1.57
0.0600	1.28	1.60
0.0700	1.52	1.57
0.0700	1.53	....
0.0800	1.16	1.57
0.2000	1.58	1.63
0.1000	1.59	1.64

In the second column of results, the third and fourth results are considerably lower than the rest of them. But it had been noticed that in these two determinations the green color of the reduced phosphorus solution had faded to the port wine shade during the cooling of the liquid and before the filtration from the undissolved zinc, while in all the other determinations the green color had persisted till the moment of filtration. This pointed to the necessity of excluding air during the cooling of the liquid, preparatory to filtration, from the undissolved zinc, and the precaution was accordingly adopted of corking the flask while cooling, first adding a little sodium carbonate to fill the flask with carbon dioxide. Results by this procedure follow.

As the flask is already filled with hydrogen gas from the solution of the zinc, and vapor from the heating of the liquid, it is perhaps unnecessary to add the sodium carbonate at the end of the reduction. In that case the flask should be corked with a one-hole cork with drawn-out glass jet, during the solution of the zinc; and the jet closed when the reduction is completed.

It was thought that results agreeing more closely and uniformly with the theoretical might be obtained by filtering through cotton wool instead of paper, as the filtration can be considerably more quickly accomplished in that way, even when much suction is used in the latter way. Results showed this to be the case, and are also given below in comparison with results by filtering through paper.

Phosphomolybdate taken.	Phosphorus present.	Filtration through paper. Phosphorus found.	Through cotton wool. Phosphorus found.
Gram.	Per cent.	Per cent.	Per cent.
0.0100	1.63	1.41	1.55
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0200	1.63	1.46	1.50
0.0200	1.63	1.48	1.60
0.0200	1.63	1.48	1.64
0.0200	1.63	....	1.63
0.0200	1.63	....	1.55
0.0200	1.63	....	1.57
0.0300	1.63	1.58	1.64
0.0300	1.63	1.57	1.63
0.0300	1.63	....	1.64
0.0300	1.63	....	1.61
0.0400	1.63	1.55	1.64
0.0400	1.63	....	1.62
0.0500	1.63	1.57	1.61
0.0600	1.63	1.57	1.64
0.0600	1.63	1.60	1.63
0.0700	1.63	1.60	1.63
0.0800	1.63	1.62	....

From these results it is seen that cotton wool is much better for use in filtering from the undissolved zinc than paper. Very little pressure is required with the former and very little cotton wool is required. A small Hirsch funnel is necessary. But the cotton wool should not be pressed down with the finger after it is wet, but sucked down by the pump. In the above experiments the filtrations through paper were also accomplished by a Hirsch funnel, smallest size. (Paper size, seven cm.)

Using cotton wool, no oxidation of the port wine, $Mo_{12}O_{19}$, solution need be feared where the amount of phosphorus present is that which in a sample of steel (one and eight-tenths grams) would be equivalent to 0.020 per cent. or over; while with percentages under 0.020 the oxidation is never greater than will make a difference of 0.001 per cent. in the result.

All the foregoing experiments were made with the use of zinc, requiring about ten minutes for solution. This supply becom-

ing exhausted, new zinc was procured which happened to dissolve much more freely in acid, and experiments were therefore made as before but using only fifteen cc. of sulphuric acid for solution of the zinc instead of thirty-five cc. as before with the first lot of zinc. Results were noticeably lower, pointing to the inference that a large excess of sulphuric acid present is necessary as favoring the stability of the $Mo_{12}O_{19}$ port wine solution. Other determinations were then made, using twenty-five cc. of acid.

Phosphorus present, 1.63 per cent.

Phosphomolybdate taken.	Fifteen cc. sulphuric acid. Phosphorus found.	Twenty-five cc. sulphuric acid. Phosphorus found.
Gram.	Per cent.	Per cent.
0.0400	1.63	....
0.0380	1.63	....
0.0350	1.62	....
0.0320	1.51	....
0.0300	1.55	1.60
0.0280	1.53	....
0.0250	1.50	1.61
0.0230	1.50	....
0.0230	1.55	1.61
0.0200	1.48	1.51
0.0200	1.55	1.55
0.0180	1.47	1.55
0.0180	1.48	....
0.0150	1.46	1.55
0.0150	....	1.55
0.0160	....	1.54
0.0140	....	1.56
0.0130	1.40	1.51
0.0100	1.40	1.51

This shows the necessity for the precaution of using plenty of sulphuric acid for solution of the zinc.

As before pointed out, results by the foregoing procedure, using all precautions, never fail of the theoretical, 1.63 per cent., or a reasonable approximation thereto, except when the amount of phosphomolybdate taken is only 0.0200 gram (equivalent to 0.018 per cent. in all steel determinations) or less, and the error in that case in a steel never amounts to more than 0.001 per cent. with about two grams of steel taken for analysis; and

the writer therefore, on the score of accuracy, prefers this method to the reductor method.

A convenience in phosphorus determinations is a Mohr burette for the sulphuric acid, attached to the sulphuric acid bottle by tubing reaching just to the zero mark of the burette according to the well known plan. The bottle should stand high, and the tubing be wide so that too much lung power will not be required to fill the burette. The delivery tube of the burette should also be of a good width, so that the acid may run quickly into the phosphorus solutions. The apparatus is also convenient for Elliott sulphur determinations, using sulphuric acid for acidifying the caustic soda sulphur solution instead of hydrochloric acid.

There is some difference of opinion among chemists as to the advisability of using sugar for reducing the manganese precipitate formed by the addition of permanganate to the boiling nitric acid solution of the steel. Sugar was originally recommended by Dr. Drown, but Mr. Clemens Jones, obtaining varying results which he attributed to its use, substituted ferrous sulphate with very satisfactory results. Dr. Dudley also states that in using sugar a different result is obtained than when ferrous sulphate is used. On the other hand, Handy and others have claimed that sugar has no harmful effect. The following tests were made by the writer:

No.	Using ferrous sulphate. Phosphorus. Per cent.	Using sugar. Phosphorus. Per cent.
Steel 618	0.017	0.018
" 620	0.018	0.018
Gray pig iron	0.719	0.720
Test bar	0.016	0.016
Steel 684	0.049	0.049
Phosphate solution	0.123	0.121

These results were considered sufficient evidence that sugar does not interfere with the precipitation of the phosphorus. Its use is more advantageous in several respects: it is cheaper than ferrous sulphate; less of it is required; it may be added to the boiling solution without fear of the solution boiling over; and it never contains phosphorus.

The merest pinch of sugar will suffice to reduce a very abundant precipitate of manganese peroxide if the boiling be continued for some time after its addition to the liquid.

For the filtration of the yellow phosphomolybdate precipitate with the aid of the pump, it is the writer's experience that nothing succeeds so well as two seven cm. Schleicher & Schüll No. 579 filter papers, folded and placed in the funnel together. The filtration may be made very rapidly, yet without any of the precipitate going through the paper.

After the solution of the yellow precipitate on the filter paper in ammonia and washing, the same filter may be used (without removal from the funnel) for another phosphomolybdate filtration, and so on for a number of consecutive determinations.

No. 579 is a very loose and porous paper. No. 589 *black ribbon* also serves.

SOME NEW COMPOUNDS OF THALLIUM.

By L. M. Dennis and Martha Doan, with Crystallographic Notes, by A. C. Gill.

Received September 4, 1896.

THALLOUS TRINITRIDE, TlN_3.

When a concentrated solution of potassium trinitride containing a little free hydronitric acid is added to a solution of thallous sulphate, a white, finely crystalline precipitate is formed. This compound is soluble in hot water, and when recrystallized from a hot aqueous solution, it separates in orthorhombic needles of a light straw color.

The thallium in this salt was determined volumetrically by means of a standard solution of potassium permanganate, according to the method of Willm.[1]

In the case of the hydronitric acid, a volumetric method also was first attempted. A weighed portion of the salt was dissolved in water and placed in a Hempel distilling bulb, which was connected by fused joints to a condenser. A separatory funnel was inserted in the neck of the distilling bulb. The hydronitric acid was set free by the addition of an excess of dilute sulphuric acid and was distilled into an Erlenmeyer flask containing a known amount of ammonia, the excess of ammonia being then deter-

[1] *Ann. chim. phys.*, (4), 5, 79.

mined by titration. It was at first difficult to drive over all of the hydronitric acid, the results being uniformly low with one exception, and in that case the distillate gave a reaction for sulphuric acid. The results continued poor in spite of various modifications which were tried, so that finally recourse was had to the gravimetric method, this not having been used before because of the explosive character of the silver trinitride. A weighed portion of the salt was dissolved in water and precipitated with a neutral silver nitrate solution. The silver trinitride was thoroughly washed by decantation with cold water, the washings being passed through a Schleicher and Schüll hardened filter No. 575. The precipitate was then transferred to the paper, the point of the filter carefully perforated and the precipitate washed through into a weighed porcelain crucible. Hydrochloric acid was then added to the contents of the crucible and the whole evaporated to dryness. By this treatment the silver trinitride is decomposed and the hydronitric acid expelled, together with the excess of hydrochloric acid. The silver chloride remaining in the crucible was then weighed, and from its weight the amount of nitrogen in the salt was computed. The results were:

		Calculated for TlN_3.	Found.
Thallium	204.18	82.9	82.87
Nitrogen	42.09	17.1	17.2
	246.27	100.0	100.07

The prism angle could be measured on the goniometer, but the end faces were too small to give good reflections. The trace of the macrodome on the prism face was measured repeatedly on the microscope stage, giving an angle of 51° 30′ with the vertical edge. The prism angle, 110 : 110 = 79° 50′. Hence the axial ratio:

$$\mathring{a} : \bar{b} : \dot{c} = 0.8366 : 1 : 1.2407.$$

The crystals were composed of many fine needles, sometimes twinned on the prism face (110), but more frequently in parallel growth. The double refraction was strong, and the plane of the optical axes is at right angles to the long direction of the needles, *i. e.*, = 0.001.

Thallous trinitride is somewhat soluble in cold water and is easily soluble in hot water. It is not explosive, resembling in this particular the trinitrides of potassium and sodium. It melts without decomposition when heated in an atmosphere of carbon dioxide. Its melting point was determined by placing some of the crystals in a small glass tube in the top of which was inserted a cork with two holes. Carbon dioxide was passed into the tube through one of these openings, and a small exit tube was inserted in the other. The tube was heated by immersing it in a bath containing an easily fusible alloy, and the temperature was measured with a carbon dioxide filled thermometer corrected by the Physikalisch-Technische Reichsanstalt of Charlottenburg. The corrected temperature at which the crystals melted was 334°.

When exposed to the sunlight, the crystals of thallous trinitride assume a dark brown appearance, which is probably due to the formation of thallous oxide. This change must be very superficial, however, as no change in weight could be detected in a sample which had been in a southern exposure for two months.

When heated in a current of dry nitrogen, thallous trinitride was easily reduced. The hydrogen on leaving the combustion tube, in which the boat containing the thallous trinitride was placed, was passed through two bulbs containing water. The aqueous solution thus obtained had a very distinct odor of ammonia, turned turmeric paper brown, and when neutralized with hydrochloric acid and allowed to spontaneously evaporate over sulphuric acid and caustic potash, it yielded crystals which under the microscope were identical with those of ammonium chloride. The ammonia found in two of the reductions in hydrogen was titrated with standard acetic acid, this acid being used in order that only the free ammonia might be neutralized and any ammonia which might be present combined with hydronitric acid would remain as such.[1]

In one case 29.83 per cent. of the nitrogen in the trinitride acid was converted into ammonia; in the other 27.37 per cent. of the nitrogen was thus changed.

[1] HN_3 is somewhat stronger than glacial acetic acid. *J. prakt. Chem.*, (2), **43**, 207.

Hydronitric acid was tested for in the aqueous solution by addition of silver nitrate to the solution in which the ammonia had been neutralized, and in each case only a trace was found. It was thought that perhaps the formation of the acid might be due to the presence of a small amount of moisture in the hydrogen, so a reduction was made with hydrogen which had been passed through a piece of moist cotton. In this case 21.55 per cent. of the nitrogen was converted into ammonia, and as before only a small amount of hydronitric acid was formed.

The highest results for the nitrogen converted into ammonia approximate one-third of the total nitrogen present, and inasmuch as only a trace of the nitrogen is found to exist in the form of hydronitric acid, it is possible that the molecule of the acid breaks down thus :[1]

$$\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!N{-}H + \begin{matrix} H \\ H \end{matrix} = N_2 + N\!\!<\!\!\begin{matrix} H \\ H \\ H \end{matrix}.$$

THALLOUS THALLIC TRINITRIDE, $TlN_3.TlN_9$.

It was thought that thallic trinitride might be obtained by the solution of freshly precipitated thallic hydroxide in hydronitric acid. The hydroxide when treated with hydronitric acid and warmed, dissolved to a clear straw-colored solution, but when the solution was allowed to stand at ordinary temperature, hydronitric acid escaped and thallic hydroxide was precipitated. Concentration of the solution was tried by placing it in a freezing mixture and removing the water as ice. From the liquid thus concentrated, bright yellow crystals separated, yet so much of the salt solution was occluded in the ice that this method proved wasteful. The best yield of crystals was obtained by dissolving the thallic hydroxide in a one and six-tenths per cent. solution of hydronitric acid and allowing the solution to stand at a temperature of about zero in a Hempel desiccator which was exhausted by means of a common suction pump. Glistening, yellow, needle-shaped crystals appeared. They were removed in five fractions, which under the microscope seemed to be alike and homogeneous.

[1] The further investigation of this reaction is now being carried on in this laboratory. D.

These sharply outlined crystals verged toward a brown color in the larger specimens. On the stage of a microscope they showed either parallel extinction, or an extinction of 42°. That is, the long direction of the crystals varied in different individuals. The crystals were probably triclinic, though there is a possibility that they furnished a case of flattening, parallel to the face of the orthorhombic pyramid. An optical axis emerged obliquely from the tabular face, showing that it was not really, as would otherwise appear, the pinacoid of an orthorhombic crystal. The plain angles were 132°, 132° and 96°. The double refraction was not very strong.

The thallium was determined by dissolving some of the crystals in dilute hydrochloric acid, reducing the thallium to the thallous condition by sulphurous acid, driving off the excess of the latter acid by heating the solution and then titrating with potassium permanganate. The nitrogen could not be determined by the method used for thallous trinitride, because the salt could not be dissolved either in water or dilute acids without evolution of hydronitric acid. For this reason the absolute method was used. We had already found that the salt was highly explosive, but the behavior of the thallous trinitride, when heated in an atmosphere of carbon dioxide, led us to attempt the decomposition of a small portion of this substance in a similar manner. A few milligrams were, accordingly, spread over the bottom of a long porcelain boat, which was placed in a combustion tube containing granular copper oxide. The tube was connected at one end to a carbon dioxide generator, and at the other to a Schiff nitrometer. The exit end of the tube was heated to redness and the heat was then run back very carefully toward the boat. Gradual decomposition of the compound, however, was not attained, for when the temperature in the neighborhood of the boat had risen but slightly, the salt exploded violently, shattering the boat and tube. Another portion of the hydronitride was then mixed with granular copper oxide and heated as before. The decomposition in this case was quiet and gradual. The nitrogen in the nitrometer amounted to 27.32 per cent. of the salt taken. It seemed possible, however, that in mixing the hydronitride with the coarse copper oxide, some of the salt

might have been decomposed by the friction, and that consequently the above per cent. of nitrogen might be too low. To ascertain if this were true, a fresh portion of copper oxide was ground very fine and was then carefully mixed with a small portion of the salt. In this way higher results were obtained.

The analysis gave:

		Calculated for TlN_6.	Found.
Thallium	204.18	70.81	70.70
Nitrogen	84.18	29.19	29.3
	288.36	100.00	100.00

If this were a simple compound, the thallium would seem to be in the bivalent condition, but as this is at variance with the usual behavior of the element, it seemed more probable that the compound is a double salt containing thallium in both the thallous and thallic condition. This supposition was confirmed by the behavior of the crystals when treated with hot water. Brown thallic hydroxide separated, and upon filtering this off and adding potassium iodide to the filtrate, a precipitate of thallous iodide resulted. Instead, however, of finding only fifty per cent. of thallium in the thallous condition, as would be required by the formula $TlN_3.TlN_9$, there was obtained 63.7 per cent. This excess of thallous thallium is doubtless due to the reduction of some of the thallic hydroxide by the hydronitric acid set free when the salt is treated with hot water.

Thallous-thallic trinitride is highly explosive, the decomposition being accomplished by a sharp report and a vivid flash of green light. The explosion can be brought about by heat, percussion or even gentle friction.

THALLOUS TELLURATE, Tl_2TeO_4.

In 1878 F. W. Clarke prepared what he supposed to be thallous tellurate by precipitating a thallous nitrate solution with ammonium tellurate.[1] The amount obtained was so small that no analysis was made.

To avoid the presence of other salts in the solution, we used a solution of thallous hydroxide and precipitated that by adding a

[1] *Ber. d. chem. Ges.*, 11, 1507.

solution of pure telluric acid. The white, flocculent precipitate which formed was washed with cold water, transferred to a filter and dried over calcium chloride.

In the analysis of this substance, the thallium was determined by the method above described. Considerable difficulty was encountered in the determination of the tellurium, the presence of thallium making it impossible to use either the potassium permanganate titration or the method recently described by Gooch.[1] The thallous tellurate was soluble in water, but the amount of water required for its solution was so great that the telluric acid could be precipitated by neither lead nor barium solutions. For these reasons the method of Kastner[2] was used, the tellurium being precipitated in alkaline solution by means of grape sugar. As some thallium separated with the tellurium, the precipitate was treated with nitric acid and the acid then driven off by evaporation. The thallous nitrate was removed by washing the residue with water and the tellurous oxide was filtered in a Gooch crucible, dried and weighed. The results were :

		Calculated for Tl_2TeO_4.	Found.
Thallium	408.39	68.13	68.17
Tellurium	127.00	21.19	21.19
Oxygen	64.00	10.68 (diff.)	10.64
	599.36	100.00	100.00

Thallous tellurate is slightly soluble in water, and it was hoped that there might be obtained from the aqueous solution crystals sufficiently well defined to admit of a comparison of them with those of thallous sulphate and thallous selenate. Unfortunately, however, it was found impossible, in spite of many and varied attempts, to obtain anything but a white amorphous powder. Even when a solution saturated at 40° was allowed to slowly cool to 15° through a period of eight days, no crystals resulted.

THALLOUS CYANPLATINITE, $Tl_2Pt(CN)_4$.

Carstanjen prepared what he reported to be thallous cyanplat-

1 *Ztschr. anorg. Chem.*, 7, 132.
2 *Ztschr. anal. Chem.*, 14, 142.

inite by neutralizing cyanplatinous acid with thallous carbonate.[1] The compound was given the formula TlCN.PtCN, although no analytical results were given.

The cyanplatinous acid used by us in the preparation of the thallium cyanplatinite was obtained according to the method of Schafarik.[2] It was neutralized by thallous hydroxide, which was prepared by precipitating a thallous sulphate solution with the calculated amount of baryta water. The crystals separated out in the form of thin plates.

A determination of the thallium and cyanogen gave the following results:

		Calculated for $Tl_2Pt(CN)_4$.	Observed.
Thallium	408.36	57.73	57.7
Platinum	195.00	27.56	...
Cyanogen	104.12	14.71	14.5
	707.48	100.00	

The crystals are nearly colorless plates, usually very thin and occurring irregularly grown together on the flat sides. The crystal system was not positively determinable from the material at hand, but is probably triclinic, possibly monoclinic with crossed dispersion. In converged polarized light, a bisectrix is seen nearly or quite normal to the large face of the plates, and the dispersion of the planes of the optic axes is remarkably strong, so that the crystals simply change color without becoming dark on rotation between crossed Nicols. The double refraction is high. The plates are bounded by crystal faces, giving them a six-sided outline, but on the material used no goniometric measurements could be made.

CORNELL UNIVERSITY,
AUGUST 1896.

[1] *J. prakt. Chem.*, 102, 144.
[2] *Ibid.*, 66, 401.

NOTES ON THE ESTIMATION OF CAFFEIN.

By W. A. Puckner.

Received September 2, 1896.

SOME time ago Gomberg published a method for the estimation of caffein, by means of Wagner's reagent,[1] wherein appear certain statements from which is to be inferred the superiority of this method over such where the caffein is shaken out of an aqueous solution by means of chloroform, and which, if true, would show that most methods now in use, give low results since but an imperfect separation of caffein is attained. Thus Spencer[2] is said to have demonstrated the difficulty with which the alkaloid is abstracted from watery solutions, he directing that at *least* seven portions of chloroform be used for this purpose, but offering no proof of the necessity for this departure from the usual direction of shaking out the liquid with three or four portions of the solvent. Spencer is at variance with Allen,[3] who investigated this matter and found that from a solution, slightly acidulated with sulphuric acid, one treatment with chloroform removed seventy to eighty-five per cent. of the amount present, while four usually effected complete extraction, especially if toward the end the solution is rendered faintly alkaline.

This agrees well with the results of my own experiments, where anhydrous caffein, in quantities from one-tenth to four-tenths gram, dissolved in fifty cc. one per cent. sulphuric acid, was shaken successively with twenty-five, ten and ten cc. chloroform, the united chloroform solution evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight. In each case the solution was shaken with a further quantity of ten cc. chloroform and the weight of the caffein so extracted ascertained as before.

Caffein taken. Gram.	Residue from first, second and third extraction. Gram.	Residue from fourth extraction. Gram.	Total per cent. recovered.
0.1285	0.1277	0.0004	99.69
0.1852	0.1820	0.0026	99.67
0.1988	0.1980	0.0002	99.69
0.2011	0.1977	0.0025	99.55
0.2559	0.2552	0.0005	99.92
0.4416	0.4355	0.0043	99.58

[1] This Journal, **18**, 331.
[2] *J. Anal. Chem.*, **4**, 390.
[3] Com. Org. Anal., **3**. Part II, 485.

This shows that the extraction of caffein from an aqueous solution presents no difficulties since, even when the solution is quite acid, practically the entire amount is obtained when four portions of chloroform are used; while, even if the fourth be omitted the results will be sufficiently correct for most purposes.

In the article referred to we are also told, although it is usually stated caffein may be shaken out of an acid solution, since its salts are broken up by water, that this is but relatively true; as a proof thereof the following is offered:

"1.0085 grams of caffein were dissolved in sixty cc. of sulphuric acid (1.10), and this solution was repeatedly shaken with chloroform, twenty-five cc. at a time:

Ten consecutive portions of chloroform gave a total of 0.3514 gram caffein.
Three additional " " " made " " 0.4859 " "
Three more " " " " " " 0.5034 " " "

Since the degree of dissociation of caffein salts is inversely proportional to the acid strength of the solution, it is to be expected that it will be extremely difficult to shake out the alkaloid from a solution containing so great a quantity of free acid; but while at times it may be advantageous to extract caffein from a solution having an acid reaction, in no instance would there seem need of a sufficient amount to render the method inapplicable; further, according to Knox and Prescott' Gomberg's method becomes uncertain under similar conditions.

In the experiments just quoted ten extractions with chloroform yielded but 34.85 per cent. of the total caffein, or on an average each treatment removed only 3.485 per cent., while the three subsequent treatments removed an additional 13.33 per cent. of the whole, or 4.44 per cent. for each extraction, *i. e.*, although the total substance in solution had been decreased by more than one third the average amount given up to chloroform increased in the 11th, 12th and 13th treatment; while in the 14th, 15th and 16th but 1.735 per cent., or on an average of 0.578 per cent. for each shaking was obtained.

Although the writer had never attempted a caffein determination under the conditions mentioned, he was, from theoretical considerations, inclined to question the figures given, and accordingly made the following experiments.

[1] Proceedings Am. Pharm. Ass., *1896*.

1.0137 gram caffein, rendered anhydrous by keeping in a desiccator over sulphuric acid until its weight remained constant, was dissolved in sixty cc. ten per cent. sulphuric acid and shaken successively with nine portions of chloroform, twenty-five cc. each; the chloroform solutions evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight.

1st	portion	of	twenty-five	cc.	yielded	a	residue	of	0.5525 gram.
2nd	"	"	"	"	"	"	"	"	0.2514 "
3rd	"	"	"	"	"	"	"	"	0.1155 "
4th	"	"	"	"	"	"	"	"	0.0535 "
5th	"	"	"	"	"	"	"	"	0.0237 "
6th	"	"	"	"	"	"	"	"	0.0114 "
7th	"	"	"	"	"	"	"	"	0.0058 "
8th	"	"	"	"	"	"	"	"	0.0029 "
9th	"	"	"	"	"	"	"	"	0.0015 "
									1.0182[1] "

In the second experiment 1.0001 gram anhydrous caffein in sixty cc. ten per cent. sulphuric acid, extracted as before, with chloroform in proportions of twenty-five cc. each:

1st,	2d and	3rd	portions	gave	a	total	residue	of	0.9086 gram.
4th,	5th and	6th	"	"	"	"	"	"	0.0854 "
7th,	8th and	9th	"	"	"	"	"	"	0.0134 "
									1.0074[1] "

The sulphuric acid used in Gomberg's experiments was designated as "(1:10)" by which it is presumed an acid containing ten per cent. by weight of sulphuric acid was meant; since, however, it was possible that sulphuric acid 1:10 *by volume* was the strength of the acid used, a determination was made with an acid with such concentration, *i. e.*, ten cc. concentrated sulphuric acid mixed with water enough to make when cold, 100 cc. In sixty cc. of this were dissolved 0.9790 gram caffein and extracted with chloroform in portions of twenty-five cc. each as before.

1st,	2nd and	3rd	portion	yielded	a	total	residue	of	0.6484 gram.
4th,	5th and	6th	"	"	"	"	"	"	0.2222 "
7th,	8th and	9th	"	"	"	"	"	"	0.0756 "
10th,	11th,	12th,	13th,	14th,	15th	and	16th	"	0.0379 "
									0.9841[1] "

[1] No explanation is offered to account for the plus error in the above. Contamination with sulphuric acid was suspected, but disproved.

As was to be expected, this confirms in a general way, the statement relative the difficulty with which caffein is shaken out of solutions containing a large proportion of sulphuric acid; in no way, however, does it agree with the data given by Gomberg, who by ten successive treatments with chloroform removed only 34.85 per cent., while my figures show that when a ten per cent. sulphuric acid was used, with but three extractions, fully ninety per cent. was recovered, and even with a still stronger acid (1 + 9 by volume), three portions of chloroform removed about sixty-five per cent.

UNIVERSITY OF ILLINOIS. SCHOOL OF PHARMACY.

CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

BY JAS. LEWIS HOWE.

Received August 27, 1896.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitrosochloride[1] (tetrachloride of Claus) with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus' experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallization resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanide are described by A. Dufet.[2]

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocya-

1 Joly: *Compt. rend.*, **108**, 854, *1889*; Howe: *J. Am. Chem. Soc.*, **16**, 388, *1894*.
2 *Compt. rend.*, (*1895*), **120**, 377.

nide formed crystallizes out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation with the following results :

1. Potassium rutheninitrosochloride, K_2RuCl_5NO, fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride, $RuCl_3$, fused with potassium cyanide gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate, K_2RuO_4, was dissolved in water and boiled with potassium cyanide. The deep orange-red solution was quickly decolorized and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallizing in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolorized, considerable of the greenish by-product being formed. From this solution there crystallized thick straw-colored hexago-

nal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method[1] of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended, until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its color had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinized to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's[2] hydrogel of cobaltocyanide and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in color, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted:

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with

[1] Weselsky, Sitzber. Akad. Wien., **60**, ii. (*1870*), 261; *Ber. d. chem. Ges.*, **2**, 588, *1869*.
[2] Jackson: *Ber. d. chem. Ges.*, **29**, 1020, *1896*.

great persistence to cotton fiber, on which it has been precipitated. It is decomposed very readily by alkalies with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid: Cadmium, white (soluble in hot acid); zinc, white; tin (both stannous and stannic), white; mercury, white; bismuth, white (insoluble in nitric acid); nickel, dirty green (changing to blue with hydrochloric acid); cobalt, pale red; platinum, yellow-green; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

It is acted on by potassium nitrite with sulphuric acid, and when neutralized gives a fugitive rose red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallization, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead

ruthenocyanide (carbonate, cyanide, etc.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral and then of barium carbonate in excess; warming, filtration, and evaporation to crystallization of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out) and decomposing with baryta water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by recrystallization nor could their yellowish tint be removed. The crystals are anhydrous while the white crystals contain three molecules of water of crystallization. On heating they explode with considerable violence while the square crystals decompose very gently. On recrystallization they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and recrystallization from water, crystals were obtained which were square, white, and in every respect, crystallographically as well as chemically, resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by

some trace of impurity. They are being further studied at present.

ANALYSIS OF POTASSIUM AND BARIUM RUTHENOCYANIDES.

Potassium ruthenocyanide, $K_4Ru(CN)_6,3H_2O$, formed by boiling a solution of potassium rutheninitrosochloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

		Per cent.
I.	Loss of water in four days standing over sulphuric acid.	10.84
II.	" " " at 120°	10.90
III.	" " " in 30 hours standing over sulphuric acid.	11.25
	Theory for $K_4Ru(CN)_6,3H_2O$. $3H_2O$ =	11.53

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $K_4Ru(CN)_6$.	Found. I.	II.	III.
Potassium	37.76	37.22	38.32	37.28
Ruthenium	24.53	23.90	24.22	24.44

This corresponds to the potassium ruthenocyanide described by Claus.

Barium ruthenocyanide, $Ba_2Ru(CN)_6,6H_2O$, (new) formed from the ordinary form of the potassium salt.

Pale straw-colored, diamond-shaped (up to one-half cm. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallization over sulphuric acid, lose five and a half molecules of water at 100° but retain one-half molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following: The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I and V) in an oxygen current, and the carbon

dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than five atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidized. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso group.

The results of several analyses are as follows:

	Theory for $Ba_2Ru(CN)_6.6H_2O$.	Found.						
		From $RuCl_3$ and KCN sol.	From $RuCl_3NO$ by fusion.			From $RuCl_3NO$ by solution.		
		I.	II.	III.	IV.	V.	VI.	VII.
Barium	42.90	....	....	....	42.46	43.32	42.27	42.54
Ruthenium	15.86	16.41 (with SiO_2)	15.67	....	15.72	17.92 (with SiO_2)	15.80	15.60
$5\frac{1}{2}H_2O$ (100°)	15.67	15.67	15.63	....	15.68	....	....	15.53
$6H_2O$ (200°)	16.83	16.68	16.85	...	16.69	16.71	16.56	16.68
5 C	9.37	....	....	....	....	....	....	....
6 C	11.23	....	....	....	....	....	....	....
C from combustion	...	....	....	9.91	9.16	9.96	....	9.98
C in residue	....	....	....	2.65	2.03	....	....	2.30
Total carbon	....	....	....	12.56	11.19	....	....	12.28

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA., June, 1896.

DIPYRIDINE METHYLENE IODIDE AND THE NON-FORMATION OF THE CORRESPONDING MONOPYRIDINE PRODUCTS.[1]

BY S. H. BAER and A. B. PRESCOTT.

Received September 7, 1896.

THE addition compound of pyridine and methylene iodide was formed in different ways, varying the conditions of mass, temperature, pressure, and time, as follows. The method of preparation recommended is that of No. V.

Preparation I.—Pyridine and methylene iodode in equimolecular proportions, reacting at laboratory temperature, for two days, form a dark-red crystalline mass. This was washed in cold alcohol, which does not dissolve it.

Preparations II and III.—The same proportions (those of a monopyridine product) were taken in reaction at 120° C. The methyl iodide for I and II was colored with free iodine, that for III was obtained colorless by distillation in vacuum. In each case the crystals, washed with cold alcohol, were dark-red. This color was not affected by treating the crystals with thiosulphate solution, and therefore not due to free iodine or to periodides.

Preparation IV.—By reaction of colorless methylene iodide, in the same proportions, with the pyridine, but without heat, an orange precipitate settles slowly. This was washed as the others.

Preparation V.—Pyridine of boiling point 118° C., and methylene iodide either colorless or tinged with iodine, in about equal molecular quantities, are placed in a flask, alcohol in volume equal to the two reacting materials is added, a return-condenser adjusted, and the heat of a water-bath applied for an hour. On cooling, long yellow needles separate out. To purify further, dissolve in hot fifty per cent. alcohol, cool, and add a little ether, when fine crystals are formed.

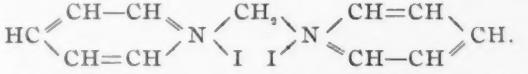
So obtained, the product is in fine needles, of yellow color, decomposing, not melting, at 220° C.; soluble in water, from which it crystallizes at 0° C.; insoluble in cold alcohol, sparingly soluble in hot alcohol; insoluble in ether, or chloroform, or benzene, or amyl alcohol; sparingly soluble in methyl alcohol.

Analysis gave us percentages as follows:

	Calculated for $(C_5H_5N)_2CH_2I_2$.	Found. I.	II.	III.	IV.	V.
I	59.61	58.95	58.91	57.98	58.4	59.6
N.....	6.57	....	....	....	...	6.72

[1] Read at the Buffalo meeting of the American Association for the Advancement of Science.

The product, therefore, not quite pure in the first four experimental preparations, is substantially the same under the different conditions employed, and with whatever excess of the diiodomethane, is always the dipyridine addition compound. And its formula, agreeing with those of its bromine homologues,[1] may be confidently written, to express the relations of the methylene group and the halogen atoms:



Kleine found[2] that trimethylamine, in combination with dihalogen substituted hydrocarbons, forms both the monammonium and the diammonium products, the former prevailing, especially when there are not more than two atoms of carbon in the halide.

It seemed now desirable to subject pyridine to various conditions of additive reaction with various dihalides, in order to know whether it can in any case form such monamine compounds as the fatty amines sometimes form.[3] Pyridine and ethylene bromide, in equal molecular proportions, were digested together in a sealed tube for two weeks, when the entire content, a crystalline mass, was dissolved in hot alcohol of ninety-five per cent., and fractionally crystallized in successive crops, washing each with cold absolute alcohol. These crops of crystals gave, of bromine, respectively, 46.15, 46.15, 46.18, and 46.03 per cent., the calculated per cent. in $(C_5H_5N)_2C_2H_4Br_2$ being 46.21.

Next pyridine with excess of ethylene bromide was digested in a pressure flask, in water-bath, with agitation. The crystallized product gave 46.26 per cent. of bromine. Finally dipyridine ethylene bromide was heated with excess of ethylene bromide in a sealed tube to 170° C. There was some charring in the mixture. By recrystallizing from it a product was obtained which gave 45.84 per cent. of bromine.

Dipyridine ethylene bromide crystallizes in colorless plates, insoluble in ether, and melting with decomposition at 295° C.

UNIVERSITY OF MICHIGAN.

[1] The ethylene bromide, (Hofmann) Davidson, 1861: *Proc. Roy. Soc.*, page 261; The trimethylene bromide, Flintermann and Prescott, 1895: *J. Am. Chem. Soc.*, **18**, 28.

[2] G. Kleine, 1894: *Chem. Centrbl.*, page 161.

[3] This in continuation of the inquiry of Flintermann and Prescott, 1895: *J. Am. Chem. Soc.*, **18**, 33.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 13.]

DETERMINATION OF THE ATOMIC MASSES OF SILVER, MERCURY AND CADMIUM BY THE ELECTROLYTIC METHOD.[1]

BY WILLETT LEPLEY HARDIN.

Received September 26, 1896.

INTRODUCTION.

A glance at the literature on the determinations of the atomic masses of silver, cadmium and mercury will show that, with the exception of cadmium, the electrolytic method has not been tried. Aside from the fact that certain errors involved in the washing and drying of the precipitates are eliminated by this method, its simplicity at once gives it preference over the usual methods of gravimetric determinations. Inasmuch as these three metals are completely precipitated from certain of their solutions by the electric current, and as it is desirable to determine the atomic mass of any element by different methods, it was thought advisable to apply this method in a redetermination of the atomic masses of these elements.

GENERAL CONSIDERATIONS.

Before taking up the different metals separately, the following general considerations may be mentioned:

1. A careful preliminary study was made in the selection of compounds. Some compounds, which from a theoretical standpoint seemed to offer certain advantages, were found by experiment not to meet the requirements of exact determinations. Salts which can be sublimed were used whenever possible; and in all cases only those salts were used which form well defined crystals.

2. All reagents used were either prepared or purified by myself and carefully tested for impurities.

3. The metals were deposited in platinum dishes of about 200 cc. capacity and about sixty-five grams in weight. When the precipitation was complete, before interrupting the current, the

[1] From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896.

solution was siphoned from the platinum dish, pure water being added at the same time; this was continued until the solvent used was completely removed from the dish. The current was then interrupted and the deposit washed several times with boiling water, with the hope of removing any occluded hydrogen. After drying, the dishes were placed in a vacuum desiccator over anhydrous calcium chloride and allowed to remain in the balance room until their temperature was the same as that of the room. Atmospheric dust was excluded from the platinum dishes during the process of deposition by means of two glass plates which formed a complete cover; the moisture which collected on this cover was washed back into the dish from time to time. The dishes were handled with nickel tongs tipped with rubber.

4. The balance used was made expressly for this work by Henry Troemner, of Philadelphia. The beam and pans were made of aluminum, the beam being about twenty centimeters long. The framework was plated with gold to prevent corrosion. The sensibility for different loads and the ratio of the length of the two arms were carefully determined. The balance is sensitive to the fortieth of a milligram, and the sensibility is almost independent of the load up to seventy-five grams. The difference in the length of the two arms is so slight that no correction need be applied. The balance was kept in a large quiet room of nearly constant temperature.

The larger weights used were made of brass and the fractions of a gram made of platinum. The weights were all previously compared against each other and standardized with reference to the largest weight. The small corrections found in comparing them were tabulated and applied to all results. The weighings were made by the method of oscillations. The temperature and barometic pressure were noted at the time of each weighing, and all weighings were reduced to a vacuum standard. As the density of the atmosphere at the time of weighing the empty platinum dish was different from that at the time of weighing the dish and deposit together, the following formula was applied to obtain the weight of the deposit *in vacuo*:

$$\left[\text{Weight of (dish + deposit)} - \frac{\text{weight of dish}\left(1+\frac{\lambda}{\Delta}-\frac{\lambda}{f}\right)}{1+\frac{\lambda'}{\Delta}-\frac{\lambda'}{f}}\right] \times \left[1+\frac{\lambda'}{\Delta'}-\frac{\lambda'}{f}\right] = \text{weight of deposit } \textit{in vacuo}.$$

Where λ = density of air at the time of weighing the empty dish.

λ' = density of air at the time of weighing the dish + deposit.

Δ = density of platinum dish.

Δ' = density of metallic deposit.

f = density of weights.

As the weights were all standardized with reference to the hundred-gram brass weight, it is evident that they must all be calculated as having the same density, equal to that of brass.

5. The atomic masses of the different elements involved in the calculation of results were taken from Clarke's latest report.[1]

PART I.

DETERMINATION OF THE ATOMIC MASS OF SILVER.

The mean of all the earlier determinations, as calculated by Clarke, gives 107.923 for the atomic mass of silver; a result almost identical with the mean (107.93; O = 16) of the determinations of Stas.

PREPARATION OF PURE METALLIC SILVER.

The silver used in this work was purified by the Stas method. Two hundred grams of silver, about ninety-nine per cent. pure, were dissolved in dilute hot nitric acid. The solution was evaporated to dryness, the nitrate heated to fusion and maintained in a fused condition until the oxides of nitrogen were no longer evolved. The residue, after cooling, was dissolved in as little cold water as possible, and after standing forty-eight hours the solution was filtered through a double filter to remove any suspended matter. The clear solution was then diluted with thirty times its volume of distilled water, and to it was added an

[1] *J. Am. Chem. Soc.*, 18, 197.

excess of pure hydrochloric acid. The silver chloride which separated was allowed to subside and was then thoroughly washed by decantation, at first with water containing a little hydrochloric acid, and finally with pure water. The precipitate was then collected on a cheese cloth filter, pressed strongly and allowed to dry. When perfectly dry, the silver chloride was powdered finely and digested for three days with aqua regia ; it was then thoroughly washed by decantation with distilled water. After obtaining the pure chloride of silver, it was necessary to purify the caustic potash and milk sugar used in reducing the chloride to the metallic state. The caustic potash was heated to the boiling point and to it was added a concentrated solution of potassium sulphide to precipitate any heavy metals which might be present. The solution was filtered and the filtrate digested for some time with freshly precipitated silver oxide and again filtered to remove the excess of potassium sulphide. The milk sugar was purified in a similar manner. The silver chloride was then placed in large porcelain dishes and covered with a solution of caustic potash and milk sugar. The dishes were placed on a water-bath and heated to a temperature of 70°–80° until the reduction to finely divided metallic silver was complete. The alkaline solution was then poured off, and the gray metallic silver was washed with distilled water until the alkaline reaction disappeared. The metal was then digested with pure dilute sulphuric acid, and finally washed with dilute ammonia water. The silver thus obtained was mixed, when dry, with five per cent. of its weight of fused borax containing ten per cent. of pure sodium nitrate. The mixture was fused in a clay crucible and the silver poured into a mold. The metal obtained in this way was almost snow white in appearance, and dissolved completely in nitric acid to a colorless solution.

PREPARATION OF PURE NITRIC ACID.

To obtain pure nitric acid, one-half liter of the commercial C. P. acid was mixed with an equal volume of concentrated C. P. sulphuric acid and distilled from a retort provided with a knee tube and condenser. The first portion of the distillate was rejected. The process was stopped when half of the

nitric acid present had been distilled over. The distillate was mixed with an equal volume of pure sulphuric acid and redistilled. The second distillate was collected in a flask, the mouth of which was closed with glass wool. When the process was complete, the flask was closed with a doubly perforated cork and placed in a water-bath at a temperature of 40°. A current of pure dry air was then conducted through the acid to remove any oxides of nitrogen. The acid was kept in a dark place.

EXPERIMENTS ON SILVER OXIDE.

If pure, dry silver oxide could be prepared, the atomic mass of silver could be compared directly with that of oxygen. A large number of experiments were made on this compound with the hope of determining the ratio of the atomic masses of these two elements.

PREPARATION OF SILVER OXIDE.

A portion of the pure metallic silver was dissolved in pure dilute nitric acid and the solution evaporated to crystallization. The crystals of silver nitrate were dissolved in pure water and to the solution was added a solution of pure sodium hydroxide, prepared by throwing pieces of metallic sodium on distilled water in a platinum dish. The twenty-five grams of silver oxide prepared in this way were washed by decantation with twenty liters of water. The material was then dried at the ordinary temperature, after which it was finely powdered and dried for twenty-four hours in an air-bath at 100°. The oxide was kept in a weighing tube in a dark place.

Several analyses were made by dissolving a weighed portion of the material in pure potassium cyanide, electrolyzing the solution and weighing the resulting metallic silver. The observations invariably gave less than ninety-five for the atomic mass of silver. The oxide was redried at a temperature of 125° and analyzed as before, but the quantity of silver obtained was far below that calculated for the compound Ag_2O. Observations were also made on material dried at 140° and 150°. The results showed that it was impossible to prepare the silver oxide in a pure, dry condition.

After making these observations, my attention was called to an article by M. Carey Lea,[1] in which were given the results of a series of analyses of silver oxide dried at different temperatures varying from 100° to 170°. These observations prove conclusively that oxygen is given off at a much lower temperature than that required to remove the last traces of moisture. From these observations and the results obtained by myself, it was evident that any further attempt to determine the atomic mass of silver from the oxide would be useless.

Although no careful study was made as to the nature of this compound, it might be added that, from my own observations, it seems very probable that the oxide contains some hydrogen in the form of hydroxyl.

FIRST SERIES.

EXPERIMENTS ON SILVER NITRATE.

The nitrate of silver seems to fulfil the conditions necessary for accurate analyses, inasmuch as it is stable and crystallizes in well defined crystals which can be fused without decomposition.

PREPARATION OF SILVER NITRATE.

The material used in these experiments was prepared by dissolving pure silver in pure aqueous nitric acid in a porcelain dish. An excess of silver was used, and after complete saturation the solution was poured off from the metal into a second dish and evaporated to crystallization. The perfectly transparent, rhombic plates of silver nitrate which separated were dissolved in pure water and recrystallized. The crystals were then carefully dried, placed in a platinum crucible which rested in a larger platinum dish and gradually heated to fusion. After cooling, the perfectly white opaque mass was broken up and placed in a ground-glass stoppered weighing tube and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The platinum dish in which the deposit was made was care-

[1] *Am. J. Sci.*, 44, 240.

fully cleaned with nitric acid and dried to constant weight. It was then placed in a desiccator over anhydrous calcium chloride, and this, together with the desiccator containing the tube of silver nitrate, was placed in the balance room, where they were allowed to remain until their temperatures were the same as that of the room. After weighing the platinum dish, the tube of silver nitrate was weighed and part of the salt removed to the dish, after which the tube was reweighed. The difference in the two weighings, of course, represented the weight of silver nitrate used in the experiment. Enough water to dissolve the nitrate was added to the dish, and then a solution of potassium cyanide, made by dissolving seventy-five grams of pure potassium cyanide in one liter of water, was added until the silver cyanide first formed was completely dissolved. The dish was then filled to within a quarter of an inch of the top with pure water and the solution electrolyzed with a gradually increasing strength of current. The following table will show the strength of current and the time through which it acted :

Time of action.	Strength of current.
2 hours	$N.D_{100} = 0.015$ amperes.
4 "	$N.D_{100} = 0.030$ "
6 "	$N.D_{100} = 0.075$ "
4 "	$N.D_{100} = 0.150$ "
4 "	$N.D_{100} = 0.400$ "

By gradually increasing the strength of current in this way the silver came down in a dense, white deposit. When the deposition was complete, before interrupting the current, the liquid was siphoned from the dish, pure water being added at the same time. This was continued until the cyanide was completely removed. The dish with the deposit was washed several times with boiling water and carefully dried. It was then placed in a desiccator and allowed to remain in the balance room until its temperature was the same as that of the room, when it was reweighed.

Weight of platinum dish = 71.27302 grams.

Weight of silver nitrate = 0.31198 grams.

Temperature, 22°.

Barometric pressure, 770 mm.

Weight of platinum dish + silver deposit = 71.47104 grams.

Temperature, 22°.
Barometric pressure, 760 mm.
Density of silver nitrate = 4.328.
" " brass weights = 8.5.
" " platinum dish = 21.4.
" " metallic silver = 10.5.
" " atmosphere at the time of weighing the empty dish and silver nitrate = 0.001212.
" " atmosphere at the time of weighing the platinum dish + silver deposit = 0.001196.

Computing on this basis we have the following :

$$0.31198\left(1+\frac{0.001212}{4.328}-\frac{0.001212}{8.5}\right)=0.31202=\text{weight of } AgNO_3 \textit{ in vacuo}.$$

$$71.27302\left[\frac{1+\frac{0.001212}{21.4}-\frac{0.001212}{8.5}}{1+\frac{0.001196}{21.4}-\frac{0.001196}{8.5}}\right]=71.27291=\text{weight of platinum dish at } 22^\circ \text{ and } 760 \text{ mm}.$$

$71.47104 - 71.27291 = 0.19813$ = weight of deposit at 22° and 760 mm.

$$0.19813\left(1+\frac{0.001196}{10.5}-\frac{0.001196}{8.5}\right)=0.19812=\text{weight of deposit } \textit{in vacuo}.$$

Taking O = 16 and N = 14.04, the atomic mass of silver $=\frac{0.19812\times 62.04}{(31202-19812)}=107.914$.

Ten observations on silver nitrate computed in the foregoing manner are as follows :

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.31202	0.19812	107.914
2	0.47832	0.30370	107.900
3	0.56742	0.36030	107.923
4	0.57728	0.36655	107.914
5	0.69409	0.44075	107.935
6	0.86367	0.54843	107.932
7	0.86811	0.55130	107.960

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
8	0.93716	0.59508	107.924
9	1.06170	0.67412	107.907
10	1.19849	0.76104	107.932

Mean = 107.924
Maximum = 107.960
Minimum = 107.900

Difference = 0.060
Probable error = ±0.005

Computing the atomic mass of silver from the total quantity of material used and metal obtained, we have 107.926.

SECOND SERIES.

EXPERIMENTS ON SILVER ACETATE.

The fact that silver forms well crystallized salts with a number of organic acids makes the comparison of the atomic mass of silver with the combined atomic masses of carbon, hydrogen, and oxygen, a matter of no great difficulty. From certain preliminary experiments, the acetate of silver seemed to fulfill the conditions necessary for accurate determinations.

PREPARATION OF SILVER ACETATE.

The purest commercial sodium acetate was dissolved in water, the solution filtered and recrystallized. After three crystallizations the material was dissolved in pure water, and to the rather concentrated solution was added a solution of silver nitrate, prepared in the manner already indicated. The white curdy precipitate which separated, after washing with cold water, was dissolved in hot water, the solution filtered and evaporated to crystallization. The silver acetate separated in brilliant sword-shaped crystals. After pouring off the solution the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. The material was allowed to remain in contact with the filters only for a short time. It was then placed in a platinum dish, and when apparently dry the crystals were broken up into a finely divided condition and dried forty-eight hours in a vacuum desiccator. This work was carried on in a darkened room, and the silver acetate obtained was

placed in a weighing tube, and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The method of operation was similar to that described under silver nitrate. After weighing the silver acetate, its aqueous or cyanide solution was electrolyzed and the weight of the resulting metallic silver determined. The results obtained from the aqueous solution were sometimes vitiated by the separation of silver peroxide at the anode. To prevent this, potassium cyanide was sometimes added. The results, however, from the two solutions were practically the same when no peroxide separated. From the aqueous solution the silver was deposited in a crystalline form. The strength of current and time of action were the same as for silver nitrate.

Ten observations on silver acetate reduced to a vacuum standard on the basis of

3.241 = density of silver acetate,
10.5 = " metallic silver,
24.4 = " platinum dish,
8.5 = " weights,

and computed for the formula $AgC_2H_3O_2$, assuming the atomic masses of carbon, hydrogen and oxygen to be 12.01, 1.008 and 16, respectively, are as follows:

	Weight of $AgC_2H_3O_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.32470	0.20987	107.904
2	0.40566	0.26223	107.949
3	0.52736	0.34086	107.913
4	0.60300	0.38976	107.921
5	0.67235	0.43455	107.896
6	0.72452	0.46830	107.916
7	0.78232	0.50563	107.898
8	0.79804	0.51590	107.963
9	0.92101	0.59532	107.925
10	1.02495	0.66250	107.923

Mean = 107.922
Maximum = 107.963
Minimum = 107.896

Difference = 0.067
Probable error = ± 0.005

Computing from the total quantity of material used and metal obtained we have 107.918 for the atomic mass of silver.

EXPERIMENTS ON SILVER SUCCINATE.

Silver succinate was prepared in a manner similar to that of silver acetate. The commercial C. P. succinic acid was recrystallized three times; the ammonium salt was then prepared and its aqueous solution precipitated with a solution of pure silver nitrates. The precipitate of silver succinate was thoroughly washed by decantation with pure water and carefully dried. After drying for several hours in an air-bath at 50°, the material was ground in an agate mortar to a finely divided powder, and was then redried for twenty-four hours in an air-bath at a temperature of 60°. The white powder obtained in this way was placed in a weighing tube and kept in a desiccator.

The method of analysis was similar to that of silver acetate. A weighed portion of the material was dissolved in a little potassium cyanide in a platinum dish. After diluting with pure water, the solution was electrolyzed and the resulting deposit weighed. The strength of current and time of action were the same as for silver nitrate. The results computed for the formula $C_4H_4O_4Ag_2$ were not constant, and were invariably from one to two units lower than those obtained from silver nitrate and silver acetate. The material was then dried at a temperature of 75°, but the results obtained were not satisfactory.

The two most probable causes for these low results are:

First, the difficulty of removing the last traces of impurities from a precipitate like that of silver succinate. The experience throughout this work has been, that, to remove all the impurities from a finely divided precipitate by washing is almost impossible.

Second, the difficulty met in drying material of this kind. This same difficulty was met in the experiments on silver oxide which, as shown by Lea, retained moisture up to 165°.

THIRD SERIES.

EXPERIMENTS ON SILVER BENZOATE.

The preceding work on silver acetate and silver succinate shows the necessity of selecting compounds which form well defined crystals. Perhaps no organic salt of silver fulfils the

conditions necessary for accurate analyses better than silver benzoate.

PREPARATION OF SILVER BENZOATE.

The purest commercial benzoic acid was resublimed three times from a porcelain dish into a glass beaker. The product thus obtained was dissolved in pure aqueous ammonia and the solution evaporated to crystallization. The ammonium salt was then dissolved in distilled water and to the solution was added a solution of pure silver nitrate. The white precipitate of silver benzoate which separated was washed with cold water; it was then dissolved in hot water, the solution filtered, and evaporated to crystallization. The salt separated in fine needles, which clung together in arborescent masses. After removing the liquid from the beaker, the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. When apparently dry they were broken up into small fragments and dried forty-eight hours in a vacuum desiccator. The material was then placed in a glass stoppered weighing tube and kept in a dark place.

MODE OF PROCEDURE.

The details of the method of operation are the same as those given under silver nitrate. A weighed portion of the material was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for silver nitrate.

Before the results could be reduced to a vacuum standard it was necessary to determine the specific gravity of silver benzoate. This was done by means of a specific gravity bottle, the liquid used being chloroform. The mean of two determinations gave 2.082 for the specific gravity of silver benzoate.

Ten results on this compound, reduced to a vacuum standard on the basis of

2.082 = density of silver benzoate,
10.5 = " " metallic silver,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $C_7H_5AgO_2$, assuming 12.01, 1.008, and 16 to be the atomic masses of carbon, hydrogen and oxygen, respectively, are as follows :

	Weight of $C_7H_5AgO_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.40858	0.19255	107.947
2	0.46674	0.21999	107.976
3	0.48419	0.22815	107.918
4	0.62432	0.29418	107.918
5	0.66496	0.31340	107.964
6	0.75853	0.35745	107.935
7	0.76918	0.36247	107.936
8	0.81254	0.38286	107.914
9	0.95673	0.45079	107.908
10	1.00840	0.47526	107.962

Mean = 107.938
Maximum = 107.976
Minimum = 107.908

Difference = 0.068
Probable error = ±0.005

Computing from the total quantity of material used and metal obtained we have 107.936 for the atomic mass of silver.

SUMMARY.

In discussing the work on the atomic mass of silver, two possible sources of error suggest themselves.

First, the hydrogen which is continually being set free in the process of electrolysis may, in part, be occluded by the metallic silver. As already pointed out, the metallic deposits were washed several times with boiling water, with the hope of removing any occluded gases ; but whether this effected a complete removal of all the occluded gases was not determined.

Second, the condensation of moisture on the platinum dish might be urged as a possible source of error. But it must be remembered that the dish was dried in the same manner each time and kept for several hours in a desiccator, and that the atmosphere inside the balance was kept dry by means of several beakers of anhydrous calcium chloride, and that the temperature of the balance room throughout the work was almost constant. Under these conditions there is but little chance of error from

different amounts of moisture condensed. Moreover, the variation in the different weighings of the same dish was very slight.

The advantages of the method are evident.

First, the great advantage of the method is its extreme simplicity.

Second, the nature of the compounds used and of metallic silver renders them well adapted to weighing.

Third, the method was such as to eliminate the errors incident to the ordinary gravimetric methods of analysis.

Of the three series, the first is probably entitled to the greatest weight. That the silver nitrate was pure and free from moisture seems beyond question. However, the close agreement of the last two series with the first indicates that the acetate and benzoate of silver were also free from moisture.

Giving equal weight to each of the three series, we have the following as the general mean computed from the separate observation :

	Atomic mass of silver.
First series	107.924
Second "	107.922
Third "	107.938
General mean =	107.928

Computing the general mean from the total quantities of material used and metal obtained we have :

	Atomic mass of silver.
First series	107.926
Second "	107.918
Third "	107.936
General mean =	107.927

Combining this with the first general mean we have 107.9275 as the final result for the atomic mass of silver.

PART II.

DETERMINATION OF THE ATOMIC MASS OF MERCURY.

From all the earlier determinations Clarke gives 200 as the

most probable value for the atomic mass of mercury, assuming oxygen equal to 16.

EXPERIMENTS ON MERCURIC OXIDE.

A large number of experiments were made with a view of determining the ratio of mercury to oxygen in mercuric oxide. The method proved to be unsatisfactory, although, apparently very good results were obtained in some preliminary experiments. The cause of this close agreement of results will be explained in the details of the work.

PREPARATION OF PURE MERCURIC OXIDE.

The purest commercial mercuric chloride was carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered, and evaporated to crystallization. The crystals were then thoroughly dried and carefully resublimed. The product obtained in this way consisted of white crystalline leaflets which dissolved completely in water. Pure sodium hydroxide was then prepared by throwing pieces of metallic sodium on pure water contained in a platinum dish. To the pure sodium hydroxide was added a solution of mercuric chloride, the former always being in excess. The yellow mercuric oxide which separated was washed for several days by decantation with hot water. The material was then dried twenty-four hours in an air-bath at 105°.

MODE OF PROCEDURE.

In a series of preliminary experiments made in the spring of 1895, a weighed portion of mercuric oxide prepared in the above manner was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the weight of the resulting metallic mercury determined. Inasmuch as the results obtained in these preliminary experiments were not reduced to a vacuum standard, it was thought advisable to weigh the empty platinum dish after removing the metallic deposit in order that the two weighings might be made under approximately the same conditions. The results for the most part agreed very closely and differed very little from the results obtained by other methods. Six observations computed for the formula HgO, assuming the atomic mass of oxygen to be 16, are as follows:

	Weight of HgO. Gram.	Weight of Hg. Gram.	Atomic mass of mercury.
1	0.26223	0.24281	200.05
2	0.23830	0.22065	200.02
3	0.23200	0.21482	200.06
4	0.14148	0.13100	200.00
5	0.29799	0.27592	200.03
6	0.19631	0.18177	200.02

Mean = 200.03.

These results were selected from a larger series. After making the above observations it was noticed that the platinum dish had gradually decreased in weight throughout the work. This decrease in weight indicated that the mercury deposit had formed an amalgam with the platinum dish, which was soluble in hot nitric acid. To ascertain whether such was the case or not the platinum dish, after weighing, was filled with a solution of the double cyanide of mercury and potassium and the solution electrolyzed. On dissolving the mercury deposit in cold nitric acid a dark colored film remained on the sides of the dish. The dish was then carefully washed, dried and reweighed, and found to be heavier than at the beginning of the operation, showing that the mercury had not been completely removed. The dark film was then dissolved in hot nitric acid and the dish again weighed. This last weight being less than that at the beginning showed that some of the platinum had been dissolved from the dish. The nitric acid solution of the dark film was evaporated to dryness and ignited to remove the mercury. The residue was dissolved in aqua regia, the solution evaporated to dryness, and enough water added to dissolve the small residue. A little concentrated ammonium chloride was then added to the solution, and the double chloride of ammonium and platinum separated as a yellow crystalline powder. This proved conclusively that the mercury deposit had united with the platinum dish to form an amalgam which was soluble in hot nitric acid. Hence the results given for mercuric oxide are of no value in determining the atomic mass of mercury.

A series of careful experiments was then made on the oxide dried at different temperatures. To avoid any error from the

amalgam which formed with each deposit, the platinum dish was weighed at the beginning of each observation, the temperature and barometric pressure being noted at the same time. The results obtained from the oxide dried at a temperature of 105° gave from 180 to 185 for the atomic mass of mercury. The material was then dried at a temperature of 125°, but the increase in the amount of mercury obtained was very slight. Finally with material dried at 150°, the results obtained for the atomic mass of mercury were all below 195°.

The most probable causes for these low results are:

First, the difficulty of removing the last traces of alkalies from the mercuric oxide.

Second, the difficulty met in the complete removal of the moisture from an amorphous precipitate. This difficulty as well as the first was referred to in the experiments on silver oxide.

Third, mercuric oxide does not form a clear solution with potassium cyanide. There seems to be a slight reduction of the oxide to the metallic state. It is difficult to determine whether this reduced portion unites completely with the metallic deposit or is partially removed in the process of washing. The latter is probably true, and it may be that a different method of analysis would give more accurate results for this compound.

FIRST SERIES.

EXPERIMENTS ON MERCURIC CHLORIDE.

The material used in this series of experiments was prepared from the commercial C. P. mercuric chloride. The product was first dissolved in water, the solution filtered and evaporated to crystallization. The crystals were dried and carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered and evaporated to crystallization. These crystals were dried as before and carefully resublimed. The material was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The method of operation was similar to that already described

under the different compounds of silver. A weighed portion of the mercuric chloride was dissolved in a little potassium cyanide and the solution electrolyzed. The deposit was washed and dried and handled in every way like the deposits of silver. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
4 hours	$N.D_{100} = 0.02$ amperes.
6 "	$N.D_{100} = 0.05$ "
6 "	$N.D_{100} = 0.10$ "
6 "	$N.D_{100} = 0.30$ "

A current of gradually increasing strength deposits the mercury in extremely small globules, which can be washed and handled more easily than the larger globules obtained by using a strong current at first. In cases where more than one-half gram of metal was deposited the strong current was allowed to act two hours longer.

Ten results on mercuric chloride reduced to a vacuum standard on the basis of

5.41 = density of mercuric chloride,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed from the formula $HgCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $HgCl_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.45932	0.33912	200.030
2	0.54735	0.40415	200.099
3	0.56002	0.41348	200.053
4	0.63586	0.46941	199.947
5	0.64365	0.47521	200.026
6	0.73281	0.54101	199.988
7	0.86467	0.63840	200.838
8	1.06776	0.78825	199.946
9	1.07945	0.79685	199.917
10	1.51402	1.11780	200.028

Mean = 200.006
Maximum = 200.099
Minimum = 199.917
Difference = 0.182
Probable error = ±0.011

Computing from the total quantity of material used and metal obtained we have 199.996 for the atomic mass of mercury.

SECOND SERIES.

EXPERIMENTS ON MERCURIC BROMIDE.

The bromine used in these experiments was prepared by distilling the commercial C. P. bromine twice over manganese dioxide. Any trace of chlorine which might be present would be removed by this method.

PREPARATION OF MERCURIC BROMIDE.

Fifty grams of metallic mercury were placed in a beaker and covered with water. Pure bromine was then added until the mercury was completely saturated. The contents of the beaker were then digested with hot water until the mercuric bromide dissolved; the solution was filtered and evaporated to crystallization. The white crystals of mercuric bromide which separated were thoroughly dried and carefully sublimed from a porcelain dish into a glass funnel. Only the middle portion of the sublimate was used in the experiments. The product obtained in this way consisted of brilliant crystalline leaflets which dissolved completely in water. The material was kept in a weighing tube in a desiccator.

MODE OF PROCEDURE.

The method of analysis was exactly like that described under mercuric chloride. A weighed portion of the mercuric bromide was dissolved in dilute potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for mercuric chloride.

Ten results on mercuric bromide reduced to a vacuum standard on the basis of

5.92 = density of mercuric bromide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $HgBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows:

	Weight of $HgBr_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.70002	0.38892	199.898
2	0.56430	0.31350	199.876
3	0.57142	0.31750	199.938
4	0.77285	0.42932	199.832
5	0.80930	0.44955	199.814
6	0.85342	0.47416	199.911
7	1.11076	0.61708	199.869
8	1.17270	0.65145	199.840
9	1.26186	0.70107	199.899
10	1.40142	0.77870	199.952

Mean = 199.883
Maximum = 199.952
Minimum = 199.814

Difference = 0.138
Probable error = ±0.010

Computing from the total quantity of material used and metal obtained, the atomic mass of mercury is 199.885.

THIRD SERIES.

EXPERIMENTS ON MERCURIC CYANIDE.

A series of observations was made on several organic salts of mercury with a view of selecting a compound suitable for atomic mass determinations. Mercuric acetate and other similar salts were found to be unstable in the air and unsuited for accurate analyses. Mercuric cyanide, on the other hand, was found to be perfectly stable and to form well defined crystals.

PREPARATION OF HYDROCYANIC ACID.

Five hundred grams of potassium ferrocyanide were placed in a two liter retort connected with a condenser. A cooled mixture of 300 grams of pure sulphuric acid and 700 cc. of distilled water was then poured into the retort and the mixture carefully heated until the hydrocyanic acid was distilled over into the receiver. The product obtained was redistilled and used immediately in the preparation of mercuric cyanide.

PREPARATION OF MERCURIC CYANIDE.

Fifty grams of mercuric oxide, prepared as already described in the experiments on mercuric oxide, were dissolved in pure, warm hydrocyanic acid. The solution was then filtered and evaporated to crystallization. The transparent crystals of mercuric cyanide which separated were dissolved in pure water and recrystallized. The product obtained by the second crystallization was quickly rinsed with cold water and dried for six hours in an air bath at a temperature of 50°. The crystals were then ground to a finely divided powder in an agate mortar and redried for twenty-four hours in an air bath at a temperature of 55°. The dry, white powder was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The mode of procedure with mercuric cyanide was somewhat different from that of the preceding experiments, in that no potassium cyanide was used in preparing the solution for electrolysis. A weighed portion of the material was dissolved in pure water in a platinum dish. When the crystals had completely dissolved, the dish was filled to within a quarter of an inch of the top with water, after which one drop of pure sulphuric acid was added. The solution was then electrolyzed and the resulting metal weighed. The strength of the current and the time of action were the same as for mercuric chloride. In the last four experiments, where rather large quantities of mercury were deposited, the strong current was allowed to act from two to six hours longer.

The results of ten experiments on mercuric cyanide, reduced to a vacuum standard on the basis of

4.0 = density of mercuric cyanide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $Hg(CN)_2$, assuming 12.01 and 14.04 to be the atomic masses of carbon and nitrogen, respectively, are as follows :

	Weight of $Hg(CN)_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.55776	0.44252	200.063
2	0.63290	0.50215	200.092
3	0.70652	0.56053	200.038
4	0.80241	0.63663	200.075
5	0.65706	0.52130	200.057
6	0.81678	0.64805	200.103
7	1.07628	0.85392	200.077
8	1.22615	0.97282	200.071
9	1.66225	1.31880	200.057
10	2.11170	1.67541	200.077

Mean = 200.071
Maximum = 200.103
Minimum = 200.038

Difference = 0.065
Probable error = 0.005

From the total quantity of material used and metal obtained, the atomic mass of mercury is 200.070.

FOURTH SERIES.

According to Faraday's law the quantities of different metals deposited from their solutions by the same current are proportional to their equivalent weights. In this series of experiments an attempt was made to determine the ratio of the atomic mass of mercury to that of silver by passing the same current through the solutions of the two metals and weighing the two resulting deposits. If the proper conditions could be obtained, this would certainly be the simplest and most direct method for comparing the equivalent weights of different metals. But so many difficulties were met that the method on the whole was not satisfactory.

In the "Revision of the Atomic Weight of Gold,"[1] Mallet made use of this method, and in a series of careful preliminary experiments determined the conditions most favorable to its application. From a number of experiments made by passing the same current through two different solutions of copper sul-

[1] *Am. Chem. J.*, 12, 182.

phate, using pure electrotype copper for both anode and cathode in each solution, Mallet found:

First.—Other conditions being the same, the difference in the quantities of metal deposited from solutions of unequal concentrations was very slight and somewhat variable, but the tendency was toward a slightly larger quantity from the more concentrated solution.

Second.—With equal quantities of metal in the two solutions and unequal quantities of free acid, the difference in the results obtained were almost insignificant and somewhat variable in direction, the tendency being toward a slightly larger quantity from the less acid solution.

Third.—Other conditions being the same, a difference in the temperature of the two solutions invariably caused a slightly larger deposit from the cooler solution.

Fourth.—Other conditions being the same, a difference in the size of the copper plates, and hence a difference in the "current density," caused a slightly greater deposit on the smaller plate.

Fifth.—A difference in the distance between the two plates did not produce a constant difference of result, but the tendency was toward a slightly larger deposit on the cathode plate farther separated from its anode.

From the foregoing experiments it is evident that the conditions most favorable to this method are, that the two solutions should be equally concentrated, of the same temperature, and should contain equal amounts of free acid, or when the double cyanides are used, equal quantities of free potassium cyanide. And, moreover, that the two cathodes and also the two anodes should be of the same size, and that the distance between the anode and cathode should be the same in both solutions. These conditions were closely observed throughout this work.

ARRANGEMENT OF APPARATUS.

The deposits in this series of experiments were made in two platinum dishes of equal capacity and equal internal area. The anode in each case consisted of a coil of rather large platinum wire, the two coils being of the same shape and size. The dishes were insulated from each other by means of two glass stands.

The platinum coils were completely immersed in the solutions and the portion of the wire near the surface of the liquid was covered with paraffin to prevent surface contact. The current, after passing through the two solutions, was allowed to pass through a hydrogen voltameter in order that its strength might be observed at any time.

In the second arrangement of apparatus the platinum dishes were made the anodes, and two pieces of platinum foil of the same shape and size were used for the cathodes. The results, however, from this second arrangement were not as satisfactory as from the first.

MODE OF PROCEDURE.

A solution of the double cyanide of silver and potassium was placed in one of the platinum dishes and a solution of the double cyanide of mercury and potassium in the other. The quantities of silver and mercury present in their solutions were approximately proportional to their equivalent weights. Each solution contained a slight excess of potassium cyanide. The dishes were placed in their positions and the anodes immersed sometime before the current was allowed to act. When the temperature of the two solutions was the same as that of the room, the connection was made and the same current allowed to pass through the two solutions. The quantity of metal deposited was never allowed to exceed one-half of the metal present in the solution at first. Before interrupting the current, the solutions were siphoned from the two platinum dishes at the same time with two siphons of the same bore. The deposits were then washed several times with boiling water, carefully dried and their weights determined. Experiments were made with currents of different strength and with solutions of various degrees of concentration. The results obtained were far from being satisfactory. The strength of current which seemed best adapted to the work was that which deposited about one-tenth of a gram of silver per hour.

From a large number of experiments, only seven results were obtained which seem of any value in determining the atomic mass of mercury. And it must be added that many others were

rejected, not because they were known to be vitiated in any way, but because the results obtained for the atomic mass of mercury differed from those obtained by other methods. It is possible that, in a large number of experiments, the condition would be more favorable in some than in others, but whether the close agreement of the results selected was due to this or to the balancing of errors, could not be determined.

Seven results computed on the basis of 107.92 for the atomic mass of silver are as follows:

	Weight of Hg. Gram.	Weight of Ag. Gram.	Atomic mass of mercury.
1	0.06126	0.06610	200.036
2	0.06190	0.06680	200.007
3	0.07814	0.08432	200.021
4	0.10361	0.11181	200.011
5	0.15201	0.16402	200.061
6	0.26806	0.28940	199.924
7	0.82808	0.89388	199.929

Mean = 199.996
Maximum = 200.061
Minimum = 199.924
Difference = 0.137

Computing from the total quantities of mercury and silver obtained, we have 199.971 for the atomic mass of mercury.

Although the cause of the large variation in the rejected observations could not be definitely determined, several sources of error suggest themselves.

First, small quantities of hydrogen were undoubtedly set free in the process of electrolysis, and unless these quantities were always equal in the two solutions, which is not probable, an error would be introduced.

Second, in some solutions an error might easily be introduced by a change in the atomicity of mercury, but in a solution of the double cyanide of mercury and potassium this change is hardly probable.

Third, the occlusion of hydrogen by the two metallic deposits would also be a possible source of error; but only small errors could be introduced in this way.

To account for the difference of several units in the results,

the source of error first mentioned seems by far the most probable.

SUMMARY.

In the discussion of the results obtained in the different series of observations on the compounds of silver, the probable sources of error and likewise the advantages of the method were pointed out. The same discussion applies equally well to the observations on mercury.

It is evident that the first three series of observations on mercury are entitled to more weight than the last series. Just why the results on mercuric bromide should be lower than those on mercuric chloride is not clear. Both compounds are certainly well adapted to atomic mass determinations, inasmuch as they can be purified by both crystallization and sublimation. The most probable impurity in mercuric bromine would be mercuric chloride, but that would tend to increase rather than lower the results. The series of observations on mercuric cyanide have, perhaps, one advantage over the others, in that no potassium cyanide was used. The results obtained in this series are still higher than those obtained from mercuric chloride and almost two-tenths of a unit higher than those obtained from mercuric bromide. However, as the same care was exercised in the purification of the material for each of the three series, and as there was no apparent error in either case, equal weight must be given to each of the three series in determining the most probable value of the atomic mass of mercury. And, as the mean of the last series is almost identical with the mean of the first three, equal weight can be given to this series without introducing any error.

Computing the general mean from the separate observations, we have:

	Atomic mass of mercury.
First series	200.006
Second "	199.883
Third "	200.071
Fourth "	199.996
General mean =	199.989

From the total quantities of material used and metal obtained, the general mean is :

	Atomic mass of mercury.
First series	199.996
Second "	199.885
Third "	200.070
Fourth "	199.971
General mean =	199.981

Combining this with the first general mean we have :

	Atomic mass of mercury.
First general mean =	199.989
Second " " =	199.981
Most probable mean of all the results =	199.985

or 200 for the atomic mass of mercury.

PART III.

DETERMINATION OF THE ATOMIC MASS OF CADMIUM.

Nine experimenters have determined the atomic mass of cadmium by many different methods, but the large variations in the results given by different chemists leave the true value of this constant still uncertain.

Stromeyer[1] gave no details of his method of operation, but found that 100 parts of cadmium combined with 14,352 parts of oxygen. On the basis of O = 16, this ratio gives 111.483 for the atomic mass of cadmium. This result is much lower than those obtained by other experimenters and is perhaps only of historical interest.

In a series of nine experiments, Von Hauer[2] determined the ratio of cadmium sulphate to cadmium sulphide. The sulphate used was purified by repeated recrystallizations and was finally dried at a temperature of 200°. After weighing the sulphate was always dried a second time and reweighed. The two weighings never differed as much as one milligram. The sulphide obtained was in each case tested for sulphate. The reduction of the sulphate to sulphide was accomplished by heating

[1] Berzelius' Lehrbuch, 5th Ed., 3, 1219.
[2] *J. prakt. Chem.*, 72, 350.

the sulphate in a current of dry hydrogen sulphide under pressure. The mean of nine observations computed on the basis O = 16 and S = 32.06 gives 111.93 for the atomic mass of cadmium. Considering the large quantity of material used each time and the precautions taken to insure accuracy, there seems to be little objection to the method.

Dumas[1] determined the ratio of cadmium chloride to metallic silver by titrating a solution containing a weighed quantity of cadmium chloride with a silver nitrate solution of known strength. The cadmium chloride was prepared by dissolving metallic cadmium in boiling hydrochloric acid. The solution was evaporated to dryness and the chloride fused for six hours in a current of hydrochloric acid gas. The mean of six determinations gives 112.24 for the atomic mass of cadmium (O = 16).

Maximum result, Cd =	112.759
Minimum " Cd =	111.756
Difference =	1.003

This large variation in the results obtained indicates the presence of impurities in the material used. In the first three experiments the cadmium was not purified; the mean of these three is Cd = 112.476. The metal used in the last three experiments was considered by Dumas to be absolutely pure; the mean of the last three results is Cd = 112.007. From the degree of purity of the cadmium chloride used in the different experiments, Dumas was inclined to reject the higher results and concluded that the true atomic mass of cadmium was about 112.

Lensen[2] prepared pure cadmium oxalate by precipitating a solution of cadmium chloride, purified by repeated crystallization, with pure oxalic acid. The precipitate was washed and carefully dried at a temperature of 150°. The mean of three results obtained by converting a weighed portion of the oxalate to oxide gives 112.06 for the atomic mass of cadmium (O = 16). The small quantity of material used in the different experiments is somewhat objectionable.

[1] *Ann. chim. phys.*, [3], 55, 158.
[2] *J. prakt. Chem.*, 79, 281.

Huntington,[1] under the direction of Cooke, determined the ratio of cadmium bromide to silver bromide and also the ratio of cadmium bromide to metallic silver. The bromide used was prepared by dissolving cadmium carbonate, which had been carefully purified, in pure hydrobromic acid. The product obtained was dried at a temperature of 200° and finally sublimed in a porcelain tube in a current of dry carbon dioxide. In the first series of experiments the silver bromide corresponding to the cadmium bromide used was weighed. The mean of eight determinations computed from the total quantity of material used and silver bromide obtained, on the basis of Ag = 107.93 and Br = 79.95 is Cd = 112.24. In the second series of experiments the quantity of metallic silver required to precipitate a known quantity of cadmium bromide was determined. The mean of eight determinations computed as in the first series gives 112.245 for the atomic mass of cadmium. The separate determinations in both series agree very closely.

Partridge[2] made three series of determinations. The first depended upon the conversion of cadmium oxalate into oxide, the second, on the reduction of the sulphate to sulphide, and the third, on the conversion of the oxalate into sulphide. The cadmium used in these experiments was purified by distilling twice *in vacuo*. Ten observations on the conversion of the oxalate into oxide, computed on the basis of O = 16 and C = 12, give 111.801 as a mean for the atomic mass of cadmium. Recalculated by Clarke,[3] on the basis of O = 16 and C = 12.005, the atomic mass of cadmium becomes 111.818. The mean of ten results obtained by reducing the sulphate to sulphide, computed on the basis of O = 16 and S = 32, gives 111.797 for the atomic mass of cadmium. Recalculated by Clarke on the basis of O = 16 and S = 32.074, the atomic mass of cadmium is 111.711. In the third series the oxalate of cadmium was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of ten determinations, computed on the basis of O = 16 and S = 32, gives 111.805 for the atomic mass of cadmium.

[1] *Proc. Amer. Acad.*, 17, 28.
[2] *Am. J. Sci.*, [3], 40, 377.
[3] *Am. Chem. J.*, 13, 34.

Recalculated by Clarke on the basis of O = 16 and S = 32.074, the mean becomes 111.589. Partridge gives 111.8 for the atomic mass of cadmium, as a mean of the three series. If the higher values for carbon and sulphur be introduced this value becomes somewhat lower.

Jones[1] determined the atomic mass of cadmium by two different methods. The first was based on the conversion of the metal into oxide, and the second on the conversion of the oxalate into oxide. The cadmium used was distilled six times *in vacuo*. The last distillate was tested spectroscopically and found to be free from impurities. In the first series of experiments a weighed portion of the pure metal was dissolved in pure nitric acid in a porcelain crucible. The solution was evaporated to dryness and the resulting cadmium nitrate ignited to oxide. The final decomposition was accomplished by means of a blast lamp. Reducing gases were carefully excluded from the crucible during the process of ignition. The weighings were all made against a tared crucible. The mean of ten observations, computed on a basis of O = 16 gives 112.07 for the atomic mass of cadmium. The different determinations agree very closely. In the second series of experiments cadmium oxalate, prepared by precipitating pure cadmium nitrate with pure oxalic acid, was converted into oxide. The material was carefully ignited until the oxalate was decomposed; it was then treated with nitric acid and again ignited in a manner similar to that described in the first series. The mean of five determinations computed on the basis of O = 16 and C = 12.003 is Cd = 111.032. From all the observations, Jones concludes that 112.07 represents very closely the atomic mass of cadmium (O = 16).

Lorimer and Smith[2] determined the ratio of the atomic mass of cadmium to that of oxygen by dissolving pure cadmium oxide in potassium cyanide and electrolyzing the solution. To obtain pure material, the commercial cadmium was dissolved in nitric acid and the solution evaporated to crystallization. The crystals of cadmium nitrate were removed from the liquid, dissolved in pure water and recrystallized. The product obtained by the

[1] *Am. Chem. J.*, 14, 261.
[2] *Ztschr. anorg. Chem.*, 1, 364.

second recrystallization was dissolved in a little water and treated with a slight excess of potassium cyanide in a platinum dish. From this solution the metallic cadmium was thrown out by means of the electric current. The nitrate obtained by dissolving the electrolytic cadmium in pure nitric acid was tested spectroscopically and found to be free from impurities. The pure cadmium nitrate was digested with ammonium hydroxide and ammonium carbonate and the resulting cadmium carbonate ignited to oxide in a platinum crucible. The method of operation was very simple, a weighed portion of the oxide was dissolved in pure potassium cyanide, the solution electrolyzed and the resulting metallic cadmium weighed. The mean of nine observations computed on the basis of O = 16 gives 112.055 for the atomic mass of cadmium.

Bucher[1] made six series of experiments. The cadmium used was purified by nine distillations *in vacuo*. The weighings were all reduced to a vacuum standard and computed on the basis of O = 16, S = 32.059, C = 12.003, Cl = 35.45, Br = 79.95, and Ag = 107.93.

In the first series cadmium oxalate, dried for fifty hours at 150°, was ignited to oxide. The mean of eight observations gives 111.89 for the atomic mass of cadmium.

In the second series, cadmium oxalate was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of four determinations is Cd = 112.15.

In the third series a weighed quantity of cadmium chloride, dried at a temperature of 300° in hydrochloric acid gas, was precipitated with silver nitrate and the resulting silver chloride weighed. The mean of twenty-one determinations is Cd = 112.39. The separate observations in this series agree very closely.

The fourth series was similar to the third, except that cadmium bromide was used instead of the chloride. The mean of five determinations is Cd = 112.38, a result almost identical with that obtained from the chloride.

In the fifth series a weighed portion of metallic cadmium was converted into sulphate, which was dried at 400° and weighed.

[1] Thesis, Johns Hopkins University, *1894*.

The excess of sulphuric acid which remained with the sulphate was estimated and its weight deducted. The only result given is Cd = 112.35.

In the last series metallic cadmium was converted into oxide by dissolving in nitric acid and igniting the resulting cadmium nitrate. The mean of two determinations made by igniting the material in a porcelain crucible gives 112.08 for the atomic mass of cadmium. Three similar determinations made with a platinum crucible gave as a mean Cd = 111.87. From a series of experiments on cadmium oxide, Bucher concluded that a correction should be applied to the last and also the first series. By making this correction, the results in these two series would be very close to those obtained from the chloride and bromide.

From all the preceding determinations Clarke gives 111.93 as the most probable value for the atomic mass of cadmium. The large variation in the results of different experimenters has not been fully explained. Some chemists think that the larger values are due to a higher degree of purity in the metallic cadmium used, and hence regard these values as being more nearly correct. But it must be remembered that the reverse is true in the experiments of Dumas. From material which had not been purified, Dumas obtained results ranging from 112.32 to 112.76 for the atomic mass of cadmium, while from material which he considered absolutely pure, the results were from 111.76 to 112.13.

PREPARATION OF PURE CADMIUM.

The metallic cadmium used in these experiments was purified by distillation in a current of hydrogen which had been passed through solutions of caustic potash, lead nitrate, potassium permanganate, and sulphuric acid. A hard glass combustion tube was heated to redness and the walls of the tube indented at two points with a three-cornered file. This divided the tube into three parts. Commercial cadmium was placed in one end of the tube and connection made with the hydrogen generator. After complete removal of the air, the tube was carefully heated in a combustion furnace until one-half of the metal had distilled over into the middle portion of the tube. The metal was cooled in a

current of hydrogen. The tube was then broken and the metal removed. The portions in the first and last sections of the tube were rejected. The middle portion was placed in a second combustion tube, similar to the first, and the distillation repeated. After three distillations the metal was examined spectroscopically and found to be free from impurities.

FIRST SERIES.

EXPERIMENTS ON CADMIUM CHLORIDE.

Dumas and Bucher have both determined the ratio of cadmium to chlorine in cadmium chloride. The results given for the atomic mass of cadmium by the latter experimenter are almost four-tenths of a unit higher than those given by the former.

PREPARATION OF CADMIUM CHLORIDE.

Hydrochloric acid was purified by first passing chlorine through the commercial C. P. acid to remove any sulphur dioxide; the excess of chlorine was removed by a current of carbon dioxide. The acid was then distilled from calcium chloride and the hydrochloric acid gas collected in pure water. Pure metallic cadmium was then dissolved in the acid and the solution evaporated to crystallization. The crystals of cadmium chloride were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube, similar to that used in the distillation of metallic cadmium, and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion, which consisted of pearly leaflets, was placed in a weighing tube and kept in a desiccator. As only a small quantity of the material could be sublimed at a time, the different analyses were made from different sublimations.

MODE OF PROCEDURE.

A weighed portion of the cadmium chloride was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was added and, after diluting to 200 cc. with pure water, the solution was electrolyzed. Before interrupting the current, the liquid was siphoned from a dish in a manner already outlined

in the experiments on silver. The metallic deposit was washed several times with boiling water and carefully dried. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
12 hours	$N.D_{100} = 0.1$ amperes.
4 "	$N.D_{100} = 0.15$ "
4 "	$N.D_{100} = 0.30$ "

The cadmium was thrown down as a dense white deposit.

Ten results on cadmium chloride reduced to a vacuum standard on the basis of:

3.3 = density of cadmium chloride,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $CdCl_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.43140	0.26422	112.054
2	0.49165	0.30112	112.052
3	0.71752	0.43942	112.028
4	0.72188	0.44208	112.021
5	0.77264	0.47319	112.036
6	0.81224	0.49742	112.023
7	0.90022	0.55135	112.041
8	1.02072	0.62505	112.002
9	1.26322	0.77365	112.041
10	1.52344	0.93314	112.078
		Mean =	112.038
		Maximum =	112.078
		Minimum =	112.002
		Difference =	0.076
		Probable error =	±0.005

From the total quantity of material used and metal obtained, we have 112.040 for the atomic mass of cadmium.

SECOND SERIES.

PREPARATION OF CADMIUM BROMIDE.

The bromine used in this series was purified as outlined in the experiments on mercuric bromide. The cadmium bromide was prepared by allowing bromine water to act on metallic cadmium for several days at the ordinary temperature. When the action

was complete, the solution was filtered and evaporated to crystallization. The crystals of cadmium bromide were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion was removed from the tube, placed in a weighing bottle and kept in a desiccator. The product obtained in this way consisted of a crystalline, pearly leaflet which dissolved immediately in water without leaving a residue.

MODE OF PROCEDURE.

The method of operation was the same as for cadmium chloride. A weighed portion of the material was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was then added and after diluting to 200 cc. the solution was electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for cadmium chloride.

Ten observations on cadmium bromide reduced to a vacuum standard on a basis of :

4.8 = density of cadmium bromide,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows :

	Weight of $CdBr_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.57745	0.23790	112.031
2	0.76412	0.31484	112.052
3	0.91835	0.37842	112.067
4	1.01460	0.41808	112.068
5	1.15074	0.47414	112.053
6	1.24751	0.51392	112.019
7	1.25951	0.51905	112.087
8	1.51805	0.62556	112.076
9	1.63543	0.67378	112.034
10	2.15342	0.88722	112.041
		Mean =	112.053
		Maximum =	112.087
		Minimum =	112.019
		Difference =	0.068
		Probable error =	±0.005

From the total quantity of material used and the metal obtained, Cd = 112.053.

THIRD SERIES.

In these experiments an attempt was made to determine the ratio of the atomic mass of cadmium to that of silver by allowing the same electric current to pass successively through solutions of the two metals and weighing the resulting deposits. The arrangement of apparatus and the details of the method were described under the mercury silver series. The results were not as satisfactory as the corresponding results obtained for mercury. A large number of determinations were made with currents of different strength and solutions of different concentration, but the results were, in most cases, far below those obtained in the first two series. A current which deposited about twelve hundredths of a gram of silver per hour seemed to give the best results. From all the observations, five results were selected which differed only about one-tenth of a unit from those of the first two series. Results selected in this way are entitled to but little weight, and perhaps should not be used in determining the general mean of all the observations.

Computed on the basis of 107.92 for the atomic mass of silver, the only admissible results are as follows:

	Weight of Ag. Gram.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.24335	0.12624	111.928
2	0.21262	0.11032	111.991
3	0.24515	0.12720	111.952
4	0.24331	0.12616	111.916
5	0.42520	0.22058	111.971

Mean = 111.952
Maximum = 111.991
Minimum = 111.916
Difference = 0.075

This method was discussed under mercury. The probable sources of error pointed out there apply equally well in the case of cadmium. Until the large variations can be accounted for

and the difficulties overcome, the method must be regarded as unsatisfactory.

SUMMARY.

Inasmuch as but one method of analysis has been used throughout this work, it is useless to discuss it here. The advantages and objections pointed out under silver apply also to cadmium.

In summing up the work on cadmium, equal weight must be given to the first two series. The last series must be considered alone and all that need be said of it is, that the results obtained for the atomic mass of cadmium never exceeded 112. In the corresponding series on mercury, the variations were in both directions from 200.

The general mean of the first two series calculated from the separate observations is :

	Atomic mass of Cd.
First series	= 112.038
Second series	= 112.053
General mean	= 112.0455

From the total quantity of material used and metal obtained we have:

	Atomic mass of Cd.
First series	= 112.040
Second series	= 112.053
General mean	= 112.0465

Combining this with the first general mean we have 112.046 as the most probable result of all the work, for the atomic mass of cadmium. This result is lower than those obtained by Huntington and Bucher, but agrees very closely with the results obtained by von Hauer, Dumas, Lensen, Jones, and Lorimer and Smith.

I wish here to express my sense of gratitude to Professor Edgar F. Smith, at whose suggestion this work was undertaken and under whose personal supervision it was carried out.

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